

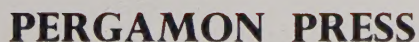
Geochimica et Cosmochimica
Acta

Executive
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JANUARY 1961

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Lead from troilite of the Toluca iron meteorite

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(Received 29 June 1960)

IN 1957 HESS, MARSHALL and UREY found that the isotopic composition of silver from troilite of the Toluca (Xiquipilco) iron meteorite was very similar to that for terrestrial silver. At the same time, they noted that the lead in this sample of troilite was quite different from the primeval lead observed by PATTERSON *et al.* (1955) in troilite from the Canyon Diablo and Henbury iron meteorites. The data on which that statement was based are presented here and some possible interpretations are offered, although the writers realize that an unique interpretation is not possible at the present time.

Lead was isolated from troilite from the Toluca meteorite in two ways. After the separation of silver from 18 g of the troilite by dithizone (HESS *et al.*, 1957), the solution was made slightly basic. Sample PbT, consisting of approximately 12 μ g of lead, was then obtained by a second dithizone extraction. Other samples (Table 1) were recovered through volatilization of the lead from the troilite. In the latter process, powdered troilite was heated in graphite crucibles at approximately 1300°C for 1 hr. The lead was recovered from the walls of a water-cooled quartz glass jacket and was further purified by dithizone extraction. The concentration of lead (second line, Table 1) was determined by volatilizing lead from the troilite together with a spike of lead rich in Pb²⁰⁶. Using an emission spectrograph, JOENSUU† found approximately 40 p.p.m. of lead in this troilite, in confirmation of the values given in Table 1.

The mass spectrometric measurement of sample T2 (Table 2) was made at Argonne National Laboratory. An accurate determination of Pb²⁰⁶/Pb²⁰⁴ ratio could not be made. The other analyses were carried out at the University of Chicago. The amount of contamination by terrestrial lead introduced during the separation of the lead from the troilite was no more than about 1 per cent for T4 (and also for T5, Table 1), and less than 0.4 per cent for PbT. Similarly, the correction of T2 for 2.7 per cent contamination would have an insignificant effect on the isotopic ratios. Differences among the sets of ratios probably reflect uncertainties in the isotopic analyses.

The simplest interpretation for the fact that the Toluca troilite lead is nearly as radiogenic as average modern lead at the surface of the earth is that the troilite may contain uranium and thorium. With the assumption that the lead originally had the isotopic composition of the primeval lead reported by PATTERSON (1955), a

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lead-lead age of $4.69 \pm 0.12 \times 10^9$ years (PbT) or $4.7_6 \pm 0.2 \times 10^9$ years (T4) can be calculated for the iron meteorite. The U^{238}/Pb^{204} ratio should be 7.2, and the concentration of uranium would have to be about 7 p.p.m. A comparable amount of thorium would also have to be present. The uncertainties are based on three times the standard errors of the mean which are listed in Table 2.

Table 1. Concentration of lead in nodule of Toluca troilite

Sample	Amount of sample (g)	Amount of lead recovered* (μ g)	Concentration of lead (p.p.m.)
T2	4.0	~ 150	> 38
T3	1.204	$77.5^\dagger$	$59^\ddagger$
		$80^\S$	> 43
T4	0.616	18	> 29
T5	0.561	14	> 25

* Colorimetric estimates, except as noted otherwise. Because the loss in separation may be as high as 50 per cent, the concentrations calculated from these estimates are minimum figures.

† Isotopic dilution experiment.

‡ Includes correction for 6.6μ g contamination Pb.

§ Includes spike lead.

Table 2. Isotopic ratios of lead from nodule of Toluca troilite*

Sample	$\frac{Pb^{204}}{Pb^{206}}$	$\frac{Pb^{207}}{Pb^{206}}$	$\frac{Pb^{208}}{Pb^{206}}$	$\frac{Pb^{206}}{Pb^{204}}$	$\frac{Pb^{207}}{Pb^{204}}$	$\frac{Pb^{208}}{Pb^{204}}$
T2	—	0.8914 ± 0.0088 (36)	2.143 ± 0.018 (35)	—	—	—
PbT	0.05831 ± 0.00082 (30)	0.8937 ± 0.0038 (24)	2.182 ± 0.009 (24)	17.15	15.33	37.42
T4	0.05806 ± 0.00069 (39)	0.9081 ± 0.0083 (28)	2.236 ± 0.025 (28)	17.22	15.64	38.51

* With standard errors of the mean and (in parentheses) numbers of ratios measured. Ratios include correction for the greater sensitivity of the multiplier to ions with higher velocity (INGRAM *et al.*, 1953). The correction is of the form

$$\frac{I_1}{I_2} (\text{corrected}) = \frac{I_1}{I_2} (\text{measured}) \sqrt{\left(\frac{M_1}{M_2}\right)}$$

where I_1 and I_2 represent two ion intensities, and M_1 and M_2 are the masses of the respective ions. The ions are assumed to be singly charged.

PATTERSON *et al.* (1953) found the Pb/U ratio in Canyon Diablo troilite to be greater than 1000. The isotopic composition of lead from the Henbury troilite (PATTERSON *et al.*, 1955) also indicates negligible amounts of uranium and thorium. Uranium concentrations of only 10^{-4} p.p.m. and less occur in the iron phase of

meteorites (REED *et al.*, 1958). Troilite in general may prove to have insignificant amounts of uranium and thorium. Such would be expected from the tendency of these elements to form oxides rather than sulphides, but as yet there are few data from troilites to confirm this impression. Toluca would seem to be an exception. If such is the case, the time of formation of this iron meteorite would coincide with that for stone meteorites as determined by a number of independent methods.

Should analyses reveal only very small concentrations of uranium and thorium in the Toluca troilite, the latter would be similar to the Holbrook chondrite in having a peculiar excess of radiogenic lead (MARSHALL and HESS, 1958; HESS and MARSHALL, 1960). In that event, another possible explanation would be the addition of lead more recently than 4.7×10^9 years ago. This lead would have to have evolved along some development line other than that for $U^{238}/Pb^{204} = 0$ (primeval lead). Assuming such to be the case, a model age (or the time elapsed since the lead became separated from uranium and thorium) of 0.77×10^9 years can be calculated from the isotopic measurement for PbT (Table 2). This value is derived from the α - β diagram for common lead (GEISS, 1954) modified by using the physical constants listed in EBERHARDT *et al.* (1955). The value of U^{238}/Pb^{204} (at today) for the development line would be 8.9. This model age would indicate that the iron meteorite was formed only about 10^9 years ago. If such were the case, variation in the isotopic composition of silver would be quite unlikely.

It is interesting to note in regard to these speculations that radiation ages for iron meteorites range from 0.5×10^9 to 1.5×10^9 years. Ages may be calculated from the potassium produced by spallation (MARSHALL, 1959). Such ages for Carbo are 1.3_8 and $1.0_5 \times 10^9$ years; for Treysa, 0.58×10^9 years; and for Clark County, $1.4_4 \times 10^9$ years, on the basis of the isotopic analyses of VOSHAGE and HINTENBERGER (1959). As these authors point out, there is a substantial and real difference between the age for Carbo ($1.3_8 \times 10^9$ years) and that for Treysa. Argon-39 and helium-3 ages for other iron meteorites (FIREMAN, 1958; FIREMAN and SCHWARZER, 1957) are close to 10^9 years, as are the potassium-argon ages for some stone meteorites. The similarity of these ages suggests that the breakup of larger bodies may have occurred at about the same time as the heating of some meteorites (MARSHALL, 1959).

Contamination by terrestrial lead could have occurred after the unobserved fall of the meteorite and before its discovery in 1776, providing that the troilite nodule was not completely enclosed by the iron. Alternatively, the troilite may have been contaminated in its separation from the iron. The latter possibility was previously admitted (HESS *et al.*, 1957, note 10) as a qualification to the subsequent extraction of silver by use of highly purified reagents. Neither of these possibilities for terrestrial contamination seems to be likely, because not only was the surface of the troilite cleaned carefully, but also the lead seemed to be homogeneously distributed throughout the nodule. Furthermore, WEDEPOHL (1956) also reports 50 p.p.m. of lead in a sample of Toluca troilite. His analyses of other troilites show that the concentration varies from about 10 p.p.m. to 60 p.p.m. Although troilite may contain as little as 5 p.p.m. of lead, concentrations ten times as great are also common.

Neither the concentration of lead nor its isotopic composition reported here

need be characteristic of all or even of most of the troilite in the Toluca meteorite. There are good grounds, however, for suspecting that it may be an important clue to the history of the iron meteorite. Because the lead contains a much smaller per cent of Pb^{204} than does primeval lead, it suggests that the Toluca iron meteorite was formed at approximately the same time as the stone meteorites, some $4.6\text{--}4.7 \times 10^9$ years ago. Nevertheless, the possibility that the meteorite may have had a more complicated history should not be overlooked.

Note added in proof

Prof. F. G. HOUTERMANS has just drawn our attention to some experiments performed more than ten years ago. At that time, Dr. H. SUESS isolated lead from another portion of the Toluca troilite, as well as from the iron phase of the meteorite. Dr. A. NIER found isotopic ratios for that lead to be similar to those reported here. Because the figures are not very different from those for common terrestrial lead, their results were ascribed to contamination in the laboratory and were never published.

Acknowledgements—We wish to thank Professors H. C. UREY and M. G. INGRAM of the University of Chicago for their kind encouragement and assistance in these experiments. This work was supported by the U.S. Atomic Energy Commission and by a grant from the U.S. National Science Foundation.

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Akzessorische Mineralien und Elemente im Serpentin von Leupoldsgrün (Münchberger Gneismasse). Ein Beitrag zur Geochemie ultrabasischer Gesteine

P. HAHN-WEINHEIMER und F. ROST

(Received 6 August, 1960)

Abstract—With the antigoritization of serpentinite near Leupoldsgrün, Oberfranken (West-Germany), caused by stress, brucite was formed intermediately. Together with magnetite, the fine-grained brucite filled numerous small joints along schistosity. The formation of brucite was followed by antigoritization and other changes in serpentinite. Simultaneously with changes in the silicate phases several phases of ore, especially magnetite, were formed.

Chemical and spectrochemical research on composition and accessory elements shows that the serpentinite of Leupoldsgrün as well as others of the "Münchberger Gneismasse" belong to the magmatic group of ultrabasic rocks. Average contents in serpentinites of Leupoldsgrün have been determined: Ni 0.243 per cent, Co 0.017 per cent, Cr 0.274 per cent. Also Pd and Pt show remarkably high values up to 0.83 p.p.m. Pd and 0.22 p.p.m. Pt.

In connexion with the geochemistry of nickel the ore mineral "Awaruit" (Ni, Fe) has been found, described and its genesis discussed.

I. EINLEITUNG

NACHDEM der eine der beiden Autoren die ultrabasischen Gesteine der Münchberger Gneismasse und ihrer zugehörigen Grünschieferzone zusammenfassend bearbeitet hatte, ohne auf spezielle Einzelheiten der zahlreichen Vorkommen näher eingehen zu können (ROST, 1956) und HAHN-WEINHEIMER (1959) anlässlich ihrer geochemischen Untersuchungen ultrabasischer und basischer Gesteine des gleichen Gebietes im Serpentin von Leupoldsgrün nicht nur überdurchschnittliche Gehalte an Platinmetallen feststellte, sondern auch aus der chemischen Analyse einer Serpentinprobe des genannten Fundortes einen unerwarteten Brucit—Gehalt berechnen konnte, sollen die mineralfaziellen und geochemischen Verhältnisse des Serpentinorkommens von Leupoldsgrün eingehender untersucht und in vorliegender Arbeit beschrieben werden.

II. LAGE UND AUFSCHLUSSVERHÄLTNISSE

Der Serpentinörper von Leupoldsgrün in Oberfranken gehört zu einem Zug der charakteristischen, zwischen die Gneise eingelagerten metamorphen Ultrabasite der Münchberger Masse, welcher deren NW-Rand von Kupferberg/Oberfranken im SW bis Epplas bei Hof im NE begleitet. Etwa $\frac{1}{2}$ km ESE des genannten Ortes bildet der Serpentin südlich der Strasse nach Konradsreuth die flache Geländeerhebung des Liebenberges und ist in einem Steinbruch auf etwa 60 m Länge gut aufgeschlossen (Abb. 1). Nach WNW zu ist der Serpentin im Liegenden deutlich massig ausgebildet und geht nach ESE zum Hangenden hin in ein zunehmend verschiefertes Gestein über. Bankung und Schieferung fallen annähernd 25–30° nach ESE bis SE ein; die dadurch ausgeprägte *s*-Fläche des Serpentinits kommt auch im Dünnschliff sowohl in einer Orientierung der Serpentinmaschenanordnung wie einer Regelung der Antigoritsschuppen zum Ausdruck (siehe auch Abb. 3).

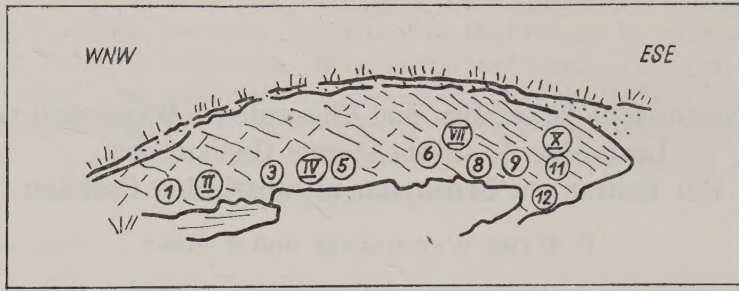


Abb. 1. Schematischer Aufriss des Steinbruchs am Liebenberg bei Leupoldgrün/Oberfranken mit den Stellen der Probeentnahme.

III. DIE UMWANDLUNGSVORGÄNGE IM SERPENTINIT

Als Ausgangsgestein für die mineralfazielle und geochemische Untersuchung der jüngeren Umwandlungsvorgänge liegt ein Serpentin vor, dessen typische Maschenstruktur als Ergebnis einer erstphasigen Hydratisierung wasserfreier Primärsilikate besonders im massigen Gestein des Westteiles weitgehend erhalten ist, ohne dass jedoch Relikte dieser Mineralien erhalten blieben. Die Maschenfaser zeigt die für die Serpentine der Münchberger Masse typische negative Elongation ($X//c$ der Faser) und kann auf Olivin als wesentlichen Primärbestandteil des Ultrabasis zurückgeführt werden. Bastitartige Strukturanordnungen deuten auf Pyroxene als weiteres Primärmineral hin, sodass der Serpentin—auch aus Vergleich mit anderen Reliktmineralien-führenden Serpentiniten des Gebietes—auf ein peridotitisches Primärgestein zurückgeführt werden kann.

Der zum Vergleich in vorliegende Untersuchung mit einbezogene Serpentin von Epplas, dessen Vorkommen nur 2,5 km NE des Liebenberges durch zahlreiche grössere Blöcke belegt ist, führt als weiteres, vorserpentinisches Mineral einen Leuchtenbergit-artigen Chlorit, der in vereinzelt Schuppen und Schuppenresten oder in Anhäufungen um die primär zu deutenden Erzkörner auftritt. In Leupoldgrün konnten nur in vereinzelt Erzkörnern kleine Chloritschuppen beobachtet werden; es ist dabei nicht zu entscheiden, ob der Chlorit in Leupoldgrün bei der Antigoritisierung verdrängt wurde oder von vornherein fehlte. Für beide Möglichkeiten finden sich in anderen Serpentiniten der Münchberger Masse Beispiele.

Der massige, vorwiegend noch in Maschenstruktur vorliegende Serpentin des Westbruches sowie die reliktschen Maschenbereiche des stärker verschieferten Ostbruches zeigen im Dünnschliff eine intensive bis ins Kleinste verzweigte Durchklüftung (Abb. 2). Die Klüftchen schwanken in ihrer Dicke von etwa 5–50 μ , im Durchschnitt 15–17 μ ; auf eine Strecke von 1 cm, senkrecht auf „s“ des Gesteins gemessen, können zwischen 50–70 dieser Klüftchen fallen, was mit dem an zahlreichen Schliffen integrierten Voluminhalt der Klüftchen von rund 10% (siehe Tabelle 2) gut übereinstimmt. Die Klüftchen sind zum Teil mit sekundärem, umgelagerten Magnetit ausgefüllt, der die Klüftchen von Rand zu Rand ganz ausfüllen oder häufig zu grösseren durchlöcherten „Platten“ zusammengelagert sein kann. Das zweite Klüftmineral ist äusserst feinkristallin und nicht fasrig; auf grund seiner höheren Lichtbrechung und Doppelbrechung gegenüber Maschen-serpentin und Antigorit, seinen zum Teil erkennbaren anomalen Interferenzfarben

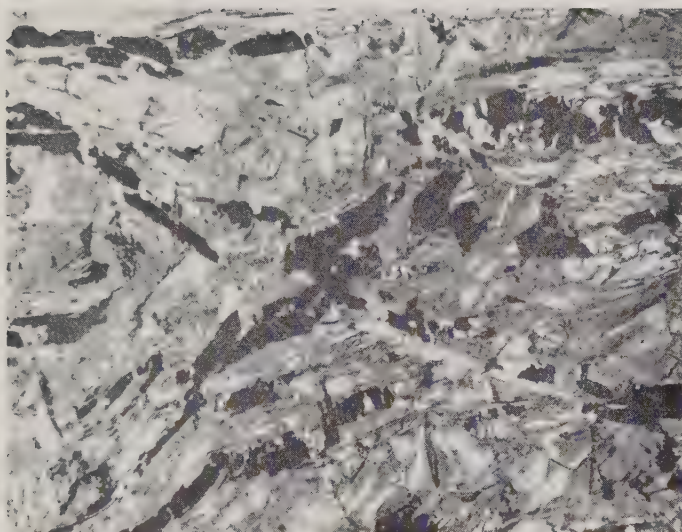


Abb. 2. Brucit-Erz-Klüftchen in reliktischem Maschenserpertinit L II von Leupoldsgrün. Brucit (hell) zwischen Magnetit-Querschnitten (schwarz); helle Schuppenquerschnitte einer beginnenden Antigoritisierung links oben und Bildmitte. Spur der *s*-Fläche und tekt. *b*-Achse horizontal. Schliff 1124; Nicols 70° gekreuzt. Bildlänge etwa 2 mm.

und aus Vergleich mit grösseren Schuppen in einer Chrysotilader wurde es als Brucit angesprochen. Einen Beweis dafür brachte sowohl die Verrechnung der chemischen Analyse in Anlehnung an die Molekular-Mesonorm von BARTH und ESKOLA (siehe Tabelle 1) als auch die röntgenographische Identifizierung, die dankenswerterweise H. JAGODZINSKI in Würzburg durchführte. Es mag in diesem Zusammenhang daran erinnert werden, dass aus dem Serpentinbruch an der Grossen Rehmühle, ebenfalls im NW-Zug der Ultrabasiteinlagerungen in der Gneismasse, Brucit in Paragenese mit Kämmererit (2–3 cm grosse Knolle) beschrieben wurde (Rost, 1956, 1960a).

Das dichteste Netzwerk der Klüftchen und damit der höchste Brucitgehalt ist in den wenig antigoritisierten Maschenserpentiniten des Westbruches zu finden, wo der Brucit-Erz-Anteil bis über 10% erreichen kann. In den stärker antigoritisierten und verschieferten Gesteinen des Bruchostteils sinkt der Volumanteil der Klüftchen unter 5%. In diesen Serpentinitten liegen zwar die Gehalte in reliktschen Maschenbereichen noch um 10%, fallen jedoch in den antigoritisierten Gesteinsanteilen auf wenige % und können stellenweise im Schliff völlig fehlen (Tabelle 2). Die quantitative Bestimmung des Volumanteils der Klüftchen durch Dünnschliffintegration kann mit den aus der Analyse berechneten Brucit-Gehalten nur grössenordnungsmässig übereinstimmen, da das Verhältnis Brucit:Erz in den Klüftchen nicht genau bestimmt werden konnte; nach Schätzung kann dieses Verhältnis Brucit:Erz zwischen 1:1 und 1:5 schwanken.

Die Frage nach der genetischen Stellung und nach dem "relativen" Alter der Brucitbildung—der Magnetitinhalt der Klüftchen ist als sekundäre Umlagerung deutbar—innerhalb der Umwandlungsvorgänge im Serpentin, die für die Geochemie ultrabasischer Gesteine von grosser Bedeutung ist, kann durch folgende Beobachtungen und Folgerungen einer Klärung zugeführt werden:

Die erste Hydratisierung des peridotitischen Primärgesteins zu Maschenserpentin ist einer absteigenden, epizonalen Metamorphose zuzuschreiben, die unter statischen Bedingungen verläuft und die in Leupoldgrün völlig durchgegriffen hat. Nach Abschluss dieser ersten Phase verursachte eine neue tektonische Bewegungsphase in der Münchberger Gneismasse im Maschenserpentin eine zunehmende "Stress"-Beanspruchung*, wobei sich (siehe auch ANGEL, 1930) die instabil gewordene Maschenfaser in Antigorit umwandeln muss. Unter Berücksichtigung der Gitterstrukturen von Chrysotil und Antigorit sowie der Annahme, dass auch in der Maschenfaser eine der Chrysotilstruktur ähnliche, aber wahrscheinlich unvollkommenere "Röllchenstruktur" vorliegt, bedeutet die—isocheme—Umwandlung der Faser-"röllchen" in die "gewellte Struktur" des Antigorits eine Gitterneuordnung, die nur über die echte Lösungsphase gehen kann. Sie führt zu einer molekulardispersen bzw. kolloiden Lösung von Magnesiumhydroxyd und hydratisierter Kieselsäure. Unter normalen Umständen kommt es bei dieser durch Verformung erzwungenen Umwandlung zu einer Neuordnung von Mg und Si im Antigoritgitter. In Leupoldgrün wurde zu Beginn der Beanspruchung jedoch auch Brucit als unlösliche Mineralphase ausgeschieden. Notwendigerweise muss die

* Diese—in unbestimmten zeitlichen Hiatus nachfolgende—tektonische Phase dürfte mit dem Beginn der letzten Aufpressung der Münchberger Masse zu identifizieren sein.

Tabelle 1. Chemische Zusammensetzung und normativer Mineralbestand

Gewichts-%	L II	L IV	L VII	L X	Epplas
SiO ₂	36,60	38,80	40,75	35,28	40,05
Al ₂ O ₃	0,54	0,49	0,19	0,66	0,61
TiO ₂	<0,02	<0,02	<0,02	<0,05	<0,02
Cr ₂ O ₃	0,26	0,20	0,20	0,25	0,23
Fe ₂ O ₃	5,27	4,79	5,64	7,27	7,35
FeO	2,59	2,35	1,11	0,67	1,49
NiO	0,31	0,27	0,33	0,34	0,33
MnO	0,10	0,07	0,10	0,07	0,05
MgO	40,62	40,95	40,50	42,10	41,50
CaO	0,14	0,14	0,17	0,13	0,21
Na ₂ O	0,06	0,24	0,53	0,03	0,18
K ₂ O	<0,05	<0,05	<0,05	<0,05	<0,05
H ₂ O +	12,84	12,75	12,45	13,31	9,72
H ₂ O -	0,61	0,51	0,47	0,64	0,30
CO ₂	0,55	0,28	0,07	0,32	0,04
S ²	<0,01	<0,01	<0,01	<0,01	<0,01
	100,57	101,92	102,59	101,17	102,14
Kationen-%					
SiO ₂	34,71	36,15	37,68	33,30	36,26
AlO _{3/2}	0,60	0,54	0,21	0,73	0,65
TiO ₂	0,01	0,01	0,01	0,03	0,01
CrO _{3/2}	0,20	0,15	0,15	0,19	0,17
FeO _{3/2}	3,75	3,35	3,91	5,15	4,99
FeO	2,05	1,83	0,86	0,53	1,13
NiO	0,23	0,21	0,24	0,26	0,24
MnO	0,08	0,06	0,08	0,06	0,04
MgO	57,35	56,74	55,61	59,12	55,89
CaO	0,14	0,14	0,17	0,13	0,24
NaO _{1/2}	0,11	0,43	0,95	0,05	0,32
CO ₂	0,71	0,36	0,09	0,41	0,05
	100,00	100,03	100,02	100,02	100,05
Molekular-Norm pro Kation (nach BARTH und ESKOLA)					
Magnetit	1,42	0,72	0,18	0,82	0,10
Or	0,30	0,30	0,30	0,30	0,30
Ab	0,55	2,15	0	0	0
An	0,70	0,13	0,38	0,65	1,20
Ac	0	0	3,80	0,20	1,28
Di	0	0,46	0,38	0	0
Serpentin	84,80	86,00	88,15	81,90	87,40
MgO (Brucit)	5,96	5,01	2,53	9,57	3,40
Erz	6,17	5,27	4,30	6,58	6,37
	99,90	100,03	100,02	100,02	100,05
Projektionswerte nach BARTH (Meso-Norm)					
Q	-25,47	-24,05	-21,98	-26,91	-22,27
Px	122,50	120,71	117,19	124,45	119,23
Fe	1,55	2,60	5,05	1,20	2,60
Brucit (Vol%)	2,5	2,1	1,05	4,0	1,4

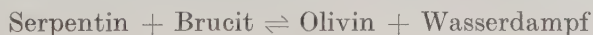
Tabelle 2. Quantitative Mineralzusammensetzung der Serpentinproben
(Numerierung siehe Abb. 1)

Probe Nr.	Maschen-serpentin	Antigorit-serpentin	Brucit-Erz-Klüftchen	Sonstige Mineralien
L 1	80	10	8,5	—
L II	60	20	11,5	0,75 "Primärerz"
L 3	60	30	7,2	0,62 "Primärerz"
L IV	24	70	5,0	—
L 5	5	90	4,3	0,4 "Primärerz"
L 6	0	80	0	20 Karbonat
L VII	28	70	0	0,57 "Primärerz"
L 8	3	95	0	1 Karbonat-Erz-Adern
L 9	5	90	0,5	1,3 "Primärerz" 1 Hornblende, 2,5 Talk
L X	20	70	4,8	—
L 11	20	75	3,8	—
L 12	0	0	0	94 Talk, 2 Chlorit 4 Sekundärerz
Epplas	12	80	< 0,5	1 Chlorit 4,5 Gesamterz

Die Zahlenwerte in Volum-% geben für Maschenserpentin und Antigorit annähernd grössenordnungsmässig das Mass der Antigoritisierung wieder.

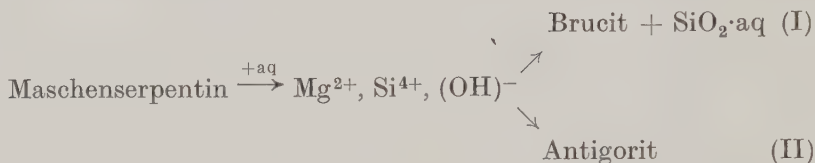
entsprechende Menge an Kieselsäure gelöst und allem Anschein nach fortgeführt worden sein.

Als erster Hinweis auf die Brucit-Bildung bei beginnender Verformung kann angeführt werden, dass die Brucit-Erz-Klüftchen nicht nur an den Maschengrenzen auftreten, sondern in die Maschensegmente vorstossen und diese durchschneiden können. Damit mag der Einwand widerlegt werden, die Brucitbildung stünde mit der ersten Serpentinisierung des Olivins in Verbindung; in diesem Fall wäre eine Beschränkung der Klüftchen auf die Maschengrenzen wahrscheinlicher. Dass grundsätzlich bei der Hydratisierung von Olivin Brucit auftreten kann, wies in neuerer Zeit DITTMANN (1960) experimentell bei seiner Untersuchung über die Metasomatose von Magnesiumsilikaten nach. Ferner gibt YODER (1952) unter Berücksichtigung der grundlegenden Arbeiten von BOWEN und TUTTLE (1949) im System $MgO-SiO_2-H_2O$ folgendes Reaktionsgleichgewicht an:



Als Hydratisierungsprodukte von Olivin können also sowohl Brucit neben kolloidaler Kieselsäure als auch Brucit neben Serpentin möglich sein.

Für die Umwandlungsvorgänge im Serpentin von Leupoldsgrün treffen beide Betrachtungen nicht zu, da als Ausgangsmaterial bereits eine hydratisierte Phase, nämlich der Maschenserpentin, vorliegt, dessen Umwandlungen nach folgendem Schema formuliert werden können:



Für die Zusammengehörigkeit von Brucit- und Antigoritbildung spricht zweitens, dass nach der Brucitbildung bei Fortdauer oder Intensivierung der Durchbewegung die Antigoritisierung folgt. Die Antigoritschuppen lagern sich zum Teil parallel an die Brucit-Erzklüftchen an, wobei eine gesetzmässige Verwachsung der Antigoritschichten (SiO_4 -Tetraeder und $\text{Mg}(\text{OH})_2$ -Oktaeder-Schichten) mit der $\text{Mg}(\text{OH})_2$ -Oktaeder-Schichtstruktur des Brucits nicht ausgeschlossen ist, da die Blättchenebene des Brucits in der Klüftchen-Ebene liegt. Zum Teil durchspiesen auch die Antigoritschuppen die Klüftchen und teilen diese bei fortgeschrittener Antigoritisierung in kleinste linsenförmige Teilbereiche auf. Die in Tabelle 2 gezeigte Abnahme des Brucit-Erz-Gehaltes in intensiver durchbewegten und antigoritiserten Serpentinpartien dürfte nach Ansicht der Verfasser damit zu erklären sein, dass hier die Neubildung des Antigorits gegenüber der Brucitbildung bevorzugt wird, also in Gleichung auf Seite die Umwandlung II vorherrscht. Denn es ist nicht wahrscheinlich, dass Brucit durch Antigorit verdrängt wird, da dieser Vorgang eine erneute Kieselsäurezufuhr erfordern würde.

Dass Brucit-Erz-Klüftchen und Antigoritneubildung demselben Verformungsplan des Serpentinits zuzuordnen sind und auch dadurch ihre Zusammengehörigkeit zeigen, wird drittens durch den Vergleich von Klüftdiagrammen der Klüftchen mit Regelungsdiagrammen der Antigoritschuppen bewiesen. Beide Diagramme (Abb. 3) zeigen nicht nur ein Maximum in der *s*-Fläche, sondern auch zwei symmetrisch zu *s* gelegene Nebenmaxima, die zu *s* einen Winkel von 15-25° bilden.

Die Durchbewegung des Serpentinits, die in Brucit-Bildung und Antigoritisierung mineralfaciellen Ausdruck fand, muss mit einer tektonischen Hebung der Münchberger Masse in seichtes Niveau verbunden gewesen sein. Denn gegen Ende der Antigoritisierung kam es im Serpentin häufig zur Bildung breiterer Klüftchen mit Chrysotilasbest, schliesslich teilweise zu einer Zerschering des Gesteinsverbandes im dm- und cm-Bereich.

Mit dem Fortdauern der Bewegungen und Hebung in seichtes tektonisches Niveau, sowie einer erneuten thermalen Tätigkeit können die Mineralneubildungen erklärt werden, die vor allem im NE-lichen Drittel des Bruches—im Bereich der Entnahmestellen 6, VII, 8, 9 und 12—weitgehende Veränderungen im Serpentin hervorriefen. In dieser Zone fehlen nicht nur die Brucit-Erz-Klüftchen, sondern es

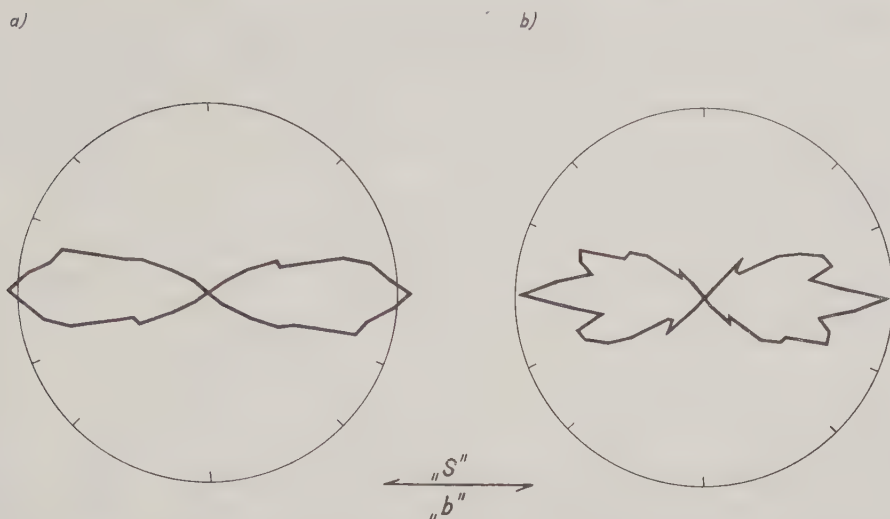


Abb. 3. Serpentin L II. Schliffage senkrecht *s* und parallel *b*. Der Vergleich des Kluftdiagramms links, in dem die Drehlagen von 1000 Bruciterzklüftchen in statistischer Verteilung über eine ganze Schlifffläche gemessen und dargestellt sind, mit dem Regelungsbild von 1000 Antigoritschuppen, analog rechts dargestellt, ergibt übereinstimmende Symmetrie des Verformungsplans.

finden sich als Reaktionsprodukte zugeführter Si- und Ca- Mengen tremolitische Hornblenden (in L 9), die sekundär grösstenteils wieder in Talk übergeführt wurden (vor allem in L 12). Dazu kommt eine sekundäre Karbonatisierung (in L 6 und L 8) und eine Umkristallisation des Magnetits zu mehr oder weniger idiomorphen Oktaedern. Diese für Serpentine nicht ungewöhnlichen Umwandlungerscheinungen sind in Leupoldsgrün in dem Teil des Gesteinskörpers lokalisiert, welcher—auch entsprechend dem Grad der Antigoritisierung—am stärksten durchbewegt wurde und dadurch den Lösungen die beste Wegsamkeit bot. Die Reaktionsbildungen in Leupoldsgrün finden eine Parallele in den Talklagerstätten der Münchberger Gneismasse (ROST, 1960b), die in gleicher charakteristischer Weise an die mehr oder weniger serpentinisierten Ultrabasite gebunden sind.

IV. ZUR GEOCHEMIE AKZESSORISCHER ELEMENTE

1. Cr, Ni und Co

In Übereinstimmung mit den Ergebnissen von VOGT (1923) bezeichnete bereits 1932 GOLDSCHMIDT (1932) Nickel und Chrom als "geochemische Leitelemente für die magmatische Herkunft basischer, magnesiumreicher Eruptivgesteine," was von EGOROVA (1938) in Erweiterung der VOGT'schen Untersuchungen bestätigt werden konnte. Zahlreiche, in der Literatur über ultrabasische Gesteine verstreuten Analysenangaben mögen weiter als Beweis für die Aussage von GOLDSCHMIDT herangezogen werden; schliesslich zeigten FAUST *et al.* (1956) neuerdings, dass die Gehalte an akzessorischen bzw. Spurenelementen zur eindeutigen Bestimmung des geologischen Ursprungs von Serpentiniten verwendet werden können, der magmatogen angenommen werden muss, wenn die Gehalte an Ni 0.01–0.4% betragen. Für Chrom gilt dieselbe Grössenordnung; es sind jedoch bei diesem

Tabelle 3. Ni, Co und Cr in Olivin und Ultrabasiten (aus GOLDSCHMIDT, 1954)

	Ni %	Co %	Cr %
Olivin			
GOLDSCHMIDT	0,08–0,4	—	0,1–0,4
WAGER und MITCHELL (1951)	0,2	—	— Früh-Olivin
Ultrabasite			
GOLDSCHMIDT (Germany)	0,36	0,024	—
NOCKOLDS und MITCHELL (1948) (Scotland)	0,065	0,020	—
SAHAMA (1945) (Finland)	<0,080	0,024	—
WAGER und MITCHELL (1951) (Greenland)	0,10	0,009	—

Element grössere Schwankungen zu erwarten, da Cr als Chromit in Ultrabasiten in unregelmässiger Verteilung vorliegt, während Ni diadoch in das Gitter der Magnesiumsilikate eingebaut wird.

Für Serpentinite der Münchberger Gneismasse liegen aus früheren Untersuchungen der beiden Verfasser zahlreiche Analysenergebnisse vor, deren Durchschnittswerte in Tabelle 4 zusammengefasst sind. Im Vergleich mit den Werten

Tabelle 4. Durchschnittswerte für Cr, Ni und Co für Serpentinite aus der zentralen Gneismasse, der Grünschieferzone und Wurlitz, Gew.-%

	Cr	Ni	Co
Zentrale Gneismasse	0,30	0,203	0,01 aus 16 Analysen (HAHN-WEINHEIMER, 1959)
Grünschieferzone	0,22	0,192	0,01 aus 10 Analysen (HAHN-WEINHEIMER, 1959)
Wurlitz	0,18	0,198	0,01 aus 38 Analysen (ROST, 1949)

für die zentrale Gneismasse liegen in den Serpentinproben von Leupoldsgrün die Gehalte von Nickel und Kobalt etwas höher (Tabelle 5); die Proben L1–L5, LX und L11 ergeben einen Durchschnittswert von 0,243% Ni und 0,017% Co. Der Durchschnittswert für Cr nähert sich mit 0,274 dem in Tabelle 4 angegebenen Gehalte der zentralen Gneismasse, während sich der von HAHN-WEINHEIMER (1959) angegebene hohe Chromgehalt nicht wieder reproduzieren liess; er ist wohl auf eine besonders Chromit-reiche Partie zurückzuführen. Auffallend ist, dass aus dem besonders stark umgewandelten Mittelteil des Serpentinikörpers L8 und L9 verminderte Ni-Gehalte besitzen, während L6, L VII und L 12 etwa den Durchschnitt erreichen. Dies kann auf eine Ni-Anreicherung während der Verwitterung zurückzuführen sein.

Die Tabellen 6 und 7 zeigen die Analysenergebnisse einiger Serpentinproben, und zwar vom Gesamtgestein (A), von dem magnetisch "enterzten" Serpentin (B)—im wesentlichen die Silikatminerale sowie gegebenenfalls Brucit und Karbonat—und von der magnetischen Fraktion (C).

Der Gesamteisengehalt ist danach in allen Serpentinproben annähernd konstant, wovon etwa 40% isomorph in Silikaten gebunden sind. Auch in diesem Zusammenhang muss auf Probe L VII hingewiesen werden, deren geringerer Eisengehalt übereinstimmend mit den Werten von L 6, L 8 und L 9 auf eine Fe-Abfuhr in diesem Teil des Gesteinskörpers hinweist (Siehe Tabelle 5). Weiter

Tabelle 5. Die Gehalte an Fe, Cr, Ni und Co in Serpentinproben von Leupoldgrün, Gew.-%

	Fe	Cr	Ni	Co	
L 1	6,2	0,14	0,24	0,022	
L II	6,0	0,26	0,26	0,019	
L 3	6,0	0,22	0,26	0,023	
L IV	5,2	0,17	0,21	0,019	
L 5	5,4	0,50	0,26	0,011	(Nr. 39 aus HAHN-WEINHEIMER, 1959)
L 6	4,1	0,31	0,23	0,009	(Nr. 40 aus HAHN-WEINHEIMER, 1959)
L VII	4,8	0,14	0,26	0,015	
L 8	4,0	0,22	0,15	0,017	
L 9	4,0	0,24	0,13	0,013	
L X	5,6	0,17	0,27	0,017	
L 11	5,4	0,18	0,20	0,008	
L 12	5,0	0,18	0,20	0,008	(Nr. 41 aus HAHN-WEINHEIMER, 1959)

Probennummern der Entnahmestellen nach Abb. 1.

erklärt sich in L VII das abweichende Verhältnis Mg/Fe in der Fraktion (B) aus dem durch Verwitterung bedingten höheren Gehalt an drei-wertigem Eisen, das nicht in silikatischer Bindung, sondern als Hämatit (und Limonit) vorliegt. Gleichfalls auf Verwitterungsvorgänge deutet das niedrige Mg/Ni-Verhältnis (mit Anreicherung des Ni).

Tabelle 6. Die Gehalte der "wesentlichen" Elemente in einigen Serpentinproben von Leupoldgrün

Probe Nr.	Magn. Anteil (Gew.-%)	% Fe	% Cr	Cr/Fe	% Ni	% Co	Co/Ni	% Mg	% Al	Mg/Fe	Mg/Ni
L IIa A		6,3	0,33	0,05	0,27	0,019	0,07	26,1	0,15	4,1	96,5
B		2,7	0,27	0,10	0,24	0,017	0,07	28,4	0,18	10,4	118,3
C	10,3	38,4	0,69	0,02	0,32	0,057	0,18	12,0	0,79	—	—
L IIb A		5,7	0,18	0,03	0,24	0,019	0,08	24,4	0,29	4,2	100,0
B		2,5	0,14	0,06	0,23	0,016	0,07	25,1	0,24	10,4	109,0
C	14,9	24,4	0,47	0,02	0,38	0,046	0,12	17,8	0,42	—	—
L IV A		5,2	0,17	0,03	0,21	0,019	0,09	24,7	0,26	4,7	117,6
B		2,4	0,16	0,07	0,21	0,019	0,09	25,6	0,25	10,6	122,0
C	8,7	35,4	0,29	0,08	0,24	0,020	0,08	13,3	0,61	—	—
L VII A		4,8	0,14	0,03	0,26	0,015	0,06	24,4	0,11	5,0	93,7
B		3,6	0,11	0,03	0,27	0,014	0,05	24,9	0,10	6,9	92,2
C	3,4	39,2	0,41	0,01	0,23	0,031	0,13	7,7	0,12	—	—
L X A		5,6	0,17	0,03	0,27	0,017	0,06	25,4	0,39	4,5	94,0
B		2,5	0,16	0,06	0,27	0,016	0,06	26,7	0,29	10,7	98,8
C	12,3	18,0	0,15	0,05	0,42	0,035	0,08	16,5	0,66	—	—
Epplas A		6,3	0,16	0,03	0,26	0,017	0,07	25,0	0,36	4,0	96,0
B		2,8	0,11	0,04	0,24	0,014	0,06	25,7	0,33	9,1	106,7
C	11,2	34,4	0,15	0,04	0,46	0,042	0,09	11,9	0,77	—	—

A: Gesamtgestein ungetrennt; B: Unmagnetischer Teil; C: Magnetischer Teil.

Der Al-Anteil der magnetischen Fraktionen liegt im allgemeinen höher als der des Gesamtgesteins, was einerseits mit der diadochen Vertretung des Fe^{3+} durch Al^{3+} im Gitter des Magnetits erklärbar ist—was auch zum Teil für Mg^{2+} und Fe^{2+} gelten kann—andererseits aber auch auf Chloritverwachsungen im Primärerz zurückgeführt werden muss, die bereits auf Seite 2 erwähnt wurden.

Zusammenfassend lassen sich die Serpentinite von Leupoldsgrün—wie auch alle anderen Ultrabasitvorkommen der Münchberger Gneismasse und der Grünschieferzone—nach Nickel-, Kobalt- und Chrom-Gehalt in die "magmatogene Gruppe" der Ultrabasite einreihen, entsprechend der Gruppe "A" nach FAUST *et al.* (1956); der Durchschnittsgehalt beträgt:

$$\text{Ni} = 0,243\% \quad \text{und} \quad \text{Co} = 0,017\%$$

entsprechend einem Verhältnis Ni/Co von 0,07.

2. Die geochemische Verteilung weiterer Elemente in den Serpentiniten von Leupoldsgrün

Erdalkalien und Alkalien zeigen in den Leupoldsgrüner Serpentinittenproben geringe Gehalte, deren Schwankungen nicht begründet werden können; nur der Na-Wert in L VII A scheint ebenfalls auf thermale Lösungszufuhr hinzuweisen.

Die Mangan-Werte liegen in den magnetisch abgetrennten Fraktionen durchweg höher und sind mit einem isomorphen Einbau des Mn im Erz zu erklären.

Von den übrigen spektralanalytisch bestimmten Elementen soll nur noch das Titan herausgegriffen werden, das im allgemeinen zwischen Silikatanteil und magnetischer Fraktion gleichmässig verteilt ist; L IIb und L X zeigen eher einen Abfall im Erzanteil. Der von allen anderen abweichende Wert in L VII C zeigt eine Titananreicherung in den—idiomorphen—Magnetiten dieser Probe, deren genetische Sonderstellung hervorzuheben ist. Bezüglich Bor und Kohlenstoff wird auf HAHN-WEINHEIMER (1960) hingewiesen.

Tabelle 7. Die Gehalte der Elemente: Ca, Sr, Ba; Na, K; Mn, Cu; Ti, Zr, V; B und C

Probe Nr.	Ca (%)	Sr (%)	Ba (%)	Na (%)	K (%)	Mn (%)	Cu (p.p.m.)	V (p.p.m.)	Ti (%)	Zr (p.p.m.)	B (p.p.m.)	C (elementar) (%)
L IIa A	0,25	0,005	0	0,016	0,08	0,072	6	18	0,01	0	20	0,008
L IIa B	—	0	0	—	—	0,069	6	—	0,01	0	—	—
L IIa C	—	0	0	—	—	0,14	0	—	0,01	0	—	—
L IIb A	0,10	0,0035	0,26	0,047	0,04	0,077	6	10	0,01	2	20	0,008
L IIb B	—	0	0,06	—	—	0,056	4	—	0,03	0	—	—
L IIb C	—	0	0	—	—	0,090	0	—	0,01	0	—	—
L IV A	0,10	0,006	0,016	0,18	0,04	0,055	9	18	0,01	0	21	0,006
L IV B	—	0	0	—	—	0,054	9	—	0,01	0	—	—
L IV C	—	0	0	—	—	0,088	0	—	0,01	0	—	—
L VII A	0,12	0,005	0	0,39	0,04	0,081	10	18	0,01	0	65	0,006
L VII B	—	0	0	—	—	0,054	7	—	0,04	0	—	—
L VII C	—	0	0	—	—	0,100	3	—	0,02	0	—	—
L X A	0,09	0,0075	0,012	0,019	0,04	0,054	10	10	0,03	0	18	0,006
L X B	—	0	0	—	—	0,046	8	—	0,03	0	—	—
L X C	—	0	0	—	—	0,085	0	—	0,01	0	—	—
A	0,10	0,0035	0,108	0,13	0,04	0,041	10	18	0,03	2	36	0,007
B	—	0	0	—	—	0,033	5	—	0,03	0	—	—
C	—	0	0	—	—	0,108	0	—	0,01	0	—	—

—: nicht bestimmt; 0: Gehalt liegt unter der Nachweisgrenze.

Tabelle 8. Gehalte an Pd und Pt im Serpentin von Leupoldsgrün (p.p.m.)

Probe Nr.	Pd	Pt
L IIa A	0,36	0,04
L IIb A	0,37	0
L VII A	0,06	0,05
L X A	0,83	0,22
Epplas A	0,14	0,10
L IV A	0,05	0,10
L IV B	0,05	0
L IV C	0,22	1,12
Durchschnitt aus 18 Analysen von Serpentin. (Münchb. Gneismasse).	0,01	0,03 (aus HAHN-WEINHEIMER, 1959)

A: Gesamtgestein; B: unmagnetischer Teil; C: magnetischer Teil.

3. Die Platinmetalle Pd und Pt

In Bestätigung des Ergebnisses von HAHN-WEINHEIMER (1959) konnten im Vergleich mit anderen Serpentinitten der Münchberger Gneismasse auch in vorliegender Untersuchung höhere Gehalte an Pd und Pt nachgewiesen werden (Tabelle 8), wobei für Platin eine Anreicherung im magnetischen Anteil (z.B. L IV C) gefunden wurde.

V. BEOBACHTUNGEN AM ERZINHALT

1. Magnetit und Chromit

Aus der mikroskopischen Dünnschliff- und besonders Anschliffuntersuchung lässt sich die Erzbildung im Serpentin in mehrere Phasen gliedern, die genetisch weitgehend mit den Silikatumwandlungen parallelisiert werden können. Als "Erz" überwiegt Magnetit, sodass die "Vererzungsphasen" in erster Linie auch als Umkristallisationen des genannten Minerals angesehen werden können.

Bereits makroskopisch sichtbar tritt der Magnetit in grösseren, unregelmässig bis rundlich geformten Körnern bis maximal 1 mm ϕ auf. Die Verteilung dieser grösseren Erzkörner ist ausserordentlich wechselnd und kann in ein und derselben Serpentinprobe, sogar in einem Schliff, grossen Schwankungen unterworfen sein. In zonar gebauten Körnern (Abb. 4) lassen sich zumindest zwei Magnetitphasen unterscheiden; eine innere "graue" Phase und eine äussere etwas heller reflektierende Phase, die wohl dem "reinen" Magnetit angehört. Aus ihr bestehen auch die späteren Magnetitbildungen (Maschenerz, Klüftchenerz und idiomorphe Erzkörner des letzten Umwandlungsstadiums) (Siehe Reflexionsmessungen in Tabelle 9). In zahlreichen grösseren Erzkörnern sind Chromitkerne vor allem im Durchlicht erkennbar, sodass es berechtigt erscheint, diese grösseren Körner als Primärerz des dunitischen bis peridotischen Ausgangsgesteins anzusehen. Sekundäre Magnetitanlagerungen an die Primärerzkörner sind zumindest da nachweisbar, wo die erzführenden Klüftchen jene berühren. Die zeitlich mit der ersten Serpentinisierung gleichzusetzende zweite Magnetitphase ist ein stets chromfreier Magnetit,

der aus einem Teil des aus dem Olivin ausgesonderten Eisens auf den Grenzen der Serpentinmaschen in Form kleiner Körnchen ausgeschieden wird und diese in charakteristischer Weise markiert ("Maschenerz"). Infolge der nachfolgenden Umwandlungen ist das Maschenerz im Serpentin von Leupoldsgrün nur noch wenig in typischer Ausbildung erhalten, sondern grösstenteils in den Magnetit der "Brucit-Erz-Klüftchen" umgelagert, der die dritte Generation des Magnetits darstellt (Siehe auch Abb. 2). Eine letzte Umlagerung des Magnetits konnte vor allem in Probe L VII beobachtet werden, auf die schon hingewiesen wurde. Hier bildet der Magnetit mehr oder weniger idiomorphe Körner von etwa $10\text{--}50\mu$ Grösse. Für ihre Herkunft kommt der Magnetit aus Maschenrändern und Klüftchen in Frage. Die grossen Primärerzkörner erfuhren in dieser Umwandlungsphase eine deutliche randliche Ankristallisation (Siehe Abb. 4).

Die Ergebnisse der Gehaltsbestimmungen akzessorischer Elemente nach den Tabellen 6 und 7 zeigen, dass im vorwiegend aus Magnetit bestehenden magnetischen Erzanteil nicht nur das Chrom beträchtlich angereichert ist, sondern dass auch Ni, Co und Mn höhere Werte aufweisen. Da der Gehalt an Schwefel—als Röstschwefel bestimmt—unter 0,01 Gew.-% liegt, ist für Ni und Co eine sulfidische Bindung zu vernachlässigen, zumal in den Anschliffen keine sulfidischen Nickelmineralien feststellbar waren, wie sie in anderen Serpentinitten beschrieben wurden (VOGT, 1923; MEIXNER, 1956). Für den Sitz des Nickels kann daher entweder Trevorit (NiFe_2O_4) als Mischkristallkomponente des Magnetits, oder Awaruit angenommen werden.

2. Awaruit

In den meisten Anschliffen und Anschliff-Körnerpräparaten der Serpentinitten von Leupoldsgrün konnte erstmalig Awaruit (Ni, Fe) aufgefunden werden. Er tritt zum Teil in feinsten Durchstäubung im Gestein auf, wobei die Partikelgrösse bis an—und wahrscheinlich unter—die Sichtbarkeitsgrenze geht, zum Teil bildet er Körner bis 0,05 mm Durchmesser, die mit Magnetit verwachsen sein können, oder skelettartige Formen in den Silikatmineralien (Abb. 5 und Abb. 6), die manchmal den Eindruck von Kluftfüllungen erwecken.

Zum Unterschied von anderen vorhandenen Erzmineralien gibt sich Awaruit im Auflicht durch eine hell-silberweisse Reflexionsfarbe zu erkennen, die mit der des Platins vergleichbar ist. Die Identifizierung wurde durch quantitative Messung des Reflexionsvermögens durchgeführt (Tabelle 9); gleichzeitig wurden Vergleichsbestimmungen an den gleichen Erzmineralien des Serpentinits von Selva bei Poschiavo, Graubünden/Schweiz vorgenommen.*

Awaruit besteht aus 70–75% Ni und 30–25% Fe, entsprechend einem Verhältnis Ni:Fe zwischen 2,3:1 bis 3:1. Da mit zunehmendem Nickelgehalt die Magnetisierbarkeit abnimmt und Awaruit in dem bearbeiteten Vorkommen sowohl mit Magnetit wie den Silikatmineralien feinst verwachsen auftreten kann, ist Awaruit in den magnetischen und unmagnetischen Fraktionen der Serpentinitten anzutreffen (Tabelle 10), wie Anschliffe von Körnerpräparaten beider Fraktionen ergaben.

* Herrn Prof. P. RAMDOHR, Heidelberg, danken wir für die Überlassung der Vergleichsprobe sowie die Bestätigung des Awaruits.

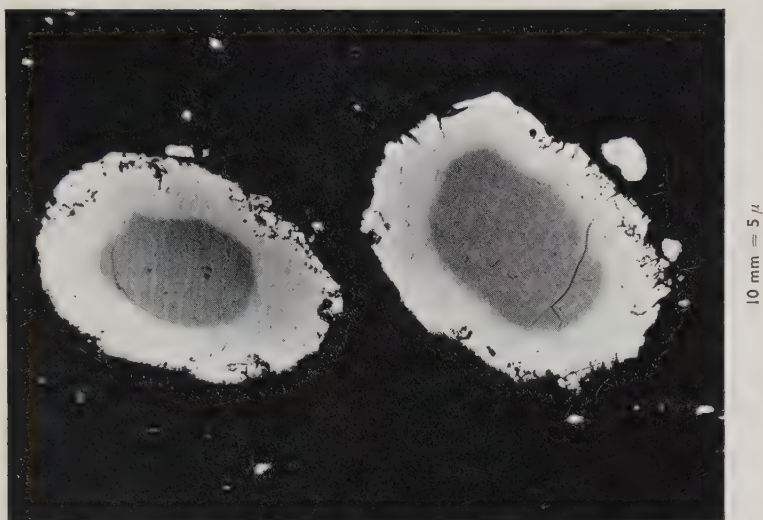


Abb. 4. Primäre Erzkörner in Serpentin von Leupoldsgrün. Chromit (dunkler Kern) wird von kompaktem, grauem Magnetit umlagert; die äussere Randzone wird von teilweise mit Silikaten verwachsenem "reinem" Magnetit gebildet. Serpentin L VII.



Abb. 5. Awaruit im Serpentin von Leupoldsgrün. Verwachsung von Awaruit (hell) mit Magnetit (grau). Serpentin L IV.



20 mm = 50 μ

Abb. 6. Awaruit im Serpentin von Leopoldgrün. Awaruit-“Skelette” neben Magnetit.
Serpentin L VII.

Tabelle 9. Reflexionsmessungen

Magnetit	Probe Nr.	In Luft		In Öl		Vergleichswert Ramdohr
		L VII	Selva	LVII gemessen	LVII berechnet	
	Photometer- okular:					
	grün	21,0	21,0	9,7	9,6	9,0
	orange	21,2	21,1	8,7	9,1	8,5
	rot	21,15	21,0	9,8–10	10,1	9,5
Awaruit	Probe Nr.	L VII	Selva	L VII	Selva	
	Photometer- okular:					
	grün	57,3	57,0	47,3	47,4	
	orange	64,6	62,7	44,4	44,4	
	rot	60,3	60,0	49,2	49,3	

Selva: Vergleichserze im Serpentin von Selva bei Poschiavo/Schweiz.

Für die Bildung des Awaruits bei hier anzunehmenden Temperaturen von $>400^{\circ}$ werden von RAMDOHR (1950) verschiedene Möglichkeiten diskutiert. Eine Entstehung aus Ni-haltigen Sulfiden—Heazlewoodit oder Pentlandit —kann für Leupoldsgrün kaum in Betracht kommen, da sulfidische Erzphasen fehlen. Bei Anwesenheit

Tabelle 10. Häufigkeit des Awaruits in nichtmagnetischer (B) und magnetischer Fraktion (C)

Probe Nr.		Awaruit
L IIa	B	(+)
	C	—
L IIb	B	+
	C	—
L IV	B	+
	C	(+)
L VII	B	+
	C	((+))
L X	B	+
	C	(+)
Epplas	B	+
	C	—

Erklärung: — nicht vorhanden; ((+)) sehr wenig vorhanden; (+) wenig vorhanden; + vorhanden.

von Schwefel erscheint die Bildung von Ni-Fe-Sulfiden gegenüber der gediegenen Phase des Awaruits bevorzugt. Dieser Ansicht steht aber die kristallchemische Erkenntnis gegenüber, dass der kovalente Bindungscharakter der Sulfide keine Voraussagen über isomorphe Vertretungen zulässt. Damit wäre für den Fall einer Anwesenheit von Schwefel die Entstehung von Awaruit nicht unmöglich.

In sulfidfreien Gesteinen nimmt RAMDOHR an, dass die Awaruitbildung am Trevorit ansetzen könnte, wobei die Reduktion durch katalytische Mitwirkung von Edelmetallspuren erfolgen solle. Nach den Ergebnissen der Anschliffuntersuchung lässt sich eine Verdrängung des "Trevorit-haltigen" Magnetits durch Awaruit oder ein Ansatz der Awaruitbildung am Magnetit nicht eindeutig belegen; Abb. 6 zeigt einerseits ein selbständiges Auftreten des Awaruits, während Abb. 5 andererseits Verwachsung mit Magnetit zeigt, die auch im Sinne einer gleichzeitigen Entstehung oder einer nachträglichen Umwachsung des Awaruits durch Magnetit interpretiert werden kann.

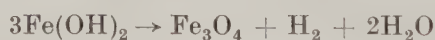
Awaruit findet sich in den metamorphen Serpentiniten häufig, wo er in demselben thermalen Bereich entsteht, in dem auch die Serpentinisierung stattfindet. Verfolgt man die Möglichkeit einer genetischen Beziehung der Serpentinisierung und der Awaruitbildung, dann ergeben sich für die Erklärung der Genese dieses Minerals folgende Anhaltspunkte:

(1) Bei der ersten Serpentinisierung von Olivin zu Serpentin wird ein Teil des diadoch eingebauten Ferro-Eisens in Magnetit übergeführt ("Maschenerz"). Zweidrittel des hierzu verbrauchten Eisens werden dabei zur drei-wertigen Form oxidiert. Nach den Berechnungen von GARRELS (1960) ist zur Bildung von Fe_3O_4 aus Fe bei 25°C und 1 atm ein O_2 -Partialdruck von 10^{-89} atm erforderlich. Bei Bildung aus FeO verringert sich der O_2 -Partialdruck auf 10^{-113} atm. Das sind so geringe Drucke, dass sie zwar experimentell nicht nachprüfbar sind, sich aber zur Beurteilung der Existenzbereiche der Eisenoxyde verwenden lassen.

(2) Die Serpentinisierung des Olivins und die Neubildung des Magnetits vollziehen sich über die reine Lösungsphase: Mg^{2+} , Si^{4+} , Fe^{2+} bzw. Fe^{3+} und Ni^{2+} sind in mehr oder weniger hydratisierter Form vorhanden.

(3) Bei Abwesenheit anderer Säuren (als Kieselsäure) darf die intermediäre hydrolytische Bildung von $\text{Fe}(\text{OH})_2$ und $\text{Ni}(\text{OH})_2$ angenommen werden.

(4) Nach der Arbeit von SHIPKO und DOUGLAS (1956) (Weitere Literaturhinweise hierzu bei LINNENBOM, 1958) setzt sich $\text{Fe}(\text{OH})_2$ bei Temperaturen über 100°C nach folgender Gleichung zu Magnetit um



Diese Umsetzung wird durch die Anwesenheit von $\text{Ni}(\text{OH})_2$ bereits unter 100°C katalysiert.

(5) Durch den hierbei gebildeten Wasserstoff ist die Reduktion des anwesenden zwei-wertigen Nickels zu Metall erklärbar. Der Partialdruck des Wasserstoffs scheint hinreichend gross zu sein, um auch einen Teil des Fe^{2+} zu reduzieren, wobei eine Aktivierung des Wasserstoffs durch Nickel denkbar ist. Dieses Eisen wird im Awaruit stabilisiert: $4\text{FeO} \rightarrow \text{Fe}_3\text{O}_4 + \text{Fe}$.

(6) Für reduzierende Verhältnisse während der Serpentinisierung und der Umwandlung des Maschenserpentins—zum Teil—in Brucit spricht auch das

Auftreten gelegentlich zu beobachtender gediegener Kupferkörnchen im Serpentin von Leupoldsgrün.

(7) Die Umsetzung von Ferroeisen zu Magnetit und Wasserstoff, der für die Awaruitbildung verantwortlich gemacht werden kann, ist zeitlich nicht nur an die erste Serpentinisierung des Olivins gebunden, sondern auch während der Brucitbildung denkbar, wenn hierbei noch einmal ein Teil des im Maschenserpentins gebundenen Ferroeisens nach obiger Gleichung (5) umgesetzt wird.

(8) Für die Beteiligung von freiem Wasserstoff an der Bildung des Awaruits kann nach STRUNZ (1957) die Beobachtung sprechen, dass im Awaruit von Grants Pass, Oregon U.S.A. reichlich H_2 (und CO_2) nachgewiesen wurden.

(9) Auch in den Serpentinproben von Leupoldsgrün konnte elementarer Wasserstoff nachgewiesen werden; verschiedene Bestimmungen ergaben für 5 g Gestein einen Gehalt von 2–20 cm³ Wasserstoff (Siehe methodischer Teil).

Vorliegende Erklärung der Awaruitbildung steht nach Auffassung der Verfasser in guter Übereinstimmung mit den petrographischen und erzmikroskopischen Beobachtungen und ordnet sich zwanglos in alle in Leupoldsgrün festgestellten metamorphen Umwandlungsvorgänge ein. Grundsätzlich kann damit die Entstehung von Awaruit auch in anderen Serpentiniten erklärt werden.

VI. METHODISCHER TEIL

1. *Vorbereitung und Probenahme*

Das dem Steinbruch entnommene, in etwa faust- bis kopfgrossen Stücken vorliegende Serpentinmaterial wurde in 2–3 cm dicke Scheiben zerschnitten; diese Scheiben wurden weiter zerteilt, sodass der von Verwitterungskrusten freie zentrale Teil zu den analytischen Bestimmungen verwendet werden konnte (rund 100 g). Direkt anschliessend an das "Analysenmaterial" wurden die zur Dünnschliff- und Anschliff-Herstellung benötigten Scheibchen abgeschnitten.

2. *Aufbereitung und Erzseparierung*

Die Aufbereitung der für die Analyse vorgesehenen Gesteinsanteile geschah in einem Labormörser mit Sinterkorundeinsatz auf 0,04–0,12 mm ϕ . Daran schloss sich die übliche Viertelung der Proben.

Die Erzseparierung wurde in dem Separator "Davis Tube" vorgenommen. Magnetfeldstärke 4800 Gauss, Magnetstromstärke 1,75 A, Magnetspannung 125 V. Durch Schlämmen im Magnetfeld liessen sich magnetische (Erz-) und unmagnetische Fraktion weiter reinigen. Es wurden jeweils 100 g Gestein verwandt und mit je 50 l Wasser geschlämmt.

3. *Analytische Bestimmungsmethoden*

SiO_2 wurde gravimetrisch nach der konventionellen Methode bestimmt.

Gesamt-Eisen und Ferroeisen wurden durch Titration mit Ce-IV-Sulfat bestimmt. Die Bestimmung von Mg und Ca erfolgte komplexometrisch, die von Na und K auf flammenspektrometrischem Wege.

Cu, Ni, Co, Cr, Mn und Ti wurden lösungsspektralanalytisch, nach Aufschluss

des Gesteins mit $\text{HF} + \text{HClO}_4$ im Teflontiegel bei 220°C , bestimmt. Die Bestimmungen von B, Ba, Sr, Zr, V und Sc erfolgten spektrochemisch durch direkte anodische Anregung der Substanz im Gemisch mit Kohlepulver im Gleichstrombogen (Harvey-Elektroden).

Bezüglich der Bestimmung von C und der Platinmetalle siehe HAHN-WEINHEIMER (1958, 1959).

Wesentlich einfacher liessen sich Fe, Cr, Ni und Co auf röntgenfluoreszenzanalytischem Wege mit einem relativen mittleren Fehler von maximal $\pm 2\%$ bestimmen. Diese Methode kam anlässlich der Kontrolle einiger Werte (Tabelle 5) zur Anwendung. Das Gesteinspulver (0,04–0,15 mm Durchmesser) wurde zu Tabletten verpresst—unter Zusatz einer verdünnten wässrigen Kunststofflösung—und die glatte Oberfläche dem Röntgenstrahl ausgesetzt. Die Intensitätsmessungen erfolgten durch Impulszählung. Die Aufstellung der Eichkurven geschah unter Berücksichtigung der Massenschwächungskoeffizienten und der Gehalte der mitangeregten Elemente.

Die Prüfung der Serpentinproben auf einen Wasserstoffgehalt wurde nach folgendem Verfahren durchgeführt: 5 g des auf 2–5 mm ϕ zerkleinerten Gesteins wurden bei 120°C in der Trockenpistole getrocknet und in einem Rohrofen gebracht. Nach Durchleiten von Reinst-Argon wurde auf 1200°C erhitzt und das entweichende Gas in eine verdünnte PdCl_2 -Lösung geleitet. Bei allen so durchgeführten Untersuchungen ergab sich eine Abscheidung von elementarem Pd. Nach Abfiltrieren und intensivem Waschen wurde das Pd in Königswasser gelöst und durch Fällung mit Chinolinselenol-2 sowie durch spektrochemischen Nachweis identifiziert. Die isolierten Pd-Mengen bewegten sich zwischen 0,01 und 0,1 mg Pd, was einer Wasserstoffmenge von 2–20 cm^3 entsprechen würde. Die Methode schliesst jedoch die Möglichkeit nicht aus, dass Wasserstoff neu gebildet wird, etwa nach (4). Seite 178.

VII. ZUSAMMENFASSUNG

Bei der durch Stress verursachten Umwandlung des Serpentinits von Leupoldsgrün/Oberfranken (Westdeutschland) bildete sich intermediär Brucit, der zusammen mit Magnetit zahlreiche, in s und flachen Scherflächen eingeregelter kleine Klüftchen erfüllte. Die Brucitbildung wird zeitlich von der Antigoritisierung abgelöst; an sie schliessen sich weitere Umwandlungen an, die hier nur kurz behandelt werden.

Die mit den verschiedenen silikatischen Umbildungen verknüpften Erzgenerationen lassen als Primärerz Chromit-(Kern) und Magnetit-Mischkristalle erkennen, sekundäre Bildungen sind im wesentlichen durch Magnetit vertreten.

Chemische und spektralanalytische Untersuchungen über Zusammensetzung und Gehalte an akzessorischen Elementen ergeben insbesondere auf grund der Ni- und Co-Werte die Zugehörigkeit des beschriebenen Serpentinits zur "magmatogenen Gruppe," in Übereinstimmung mit den anderen serpentinisierten Ultrabasiten der Münchberger Gneismasse (Durchschnittsgehalte für Leupoldsgrün: Ni 0,243%, Co 0,017%, Cr 0,274%); höhere Pd- und Pt-Gehalte von maximal 0,83 p.p.m. Pd und 0,22 p.p.m. Pt verdienen Beachtung.

Als neu beobachtete Erzkomponente wird Awaruit beschrieben; seine Bildung wird mit den anderen beobachteten Umwandlungen in Zusammenhang gebracht.

Anerkennungen—Vorliegende Untersuchungen wurden in gemeinschaftlicher Arbeit an den Mineralogischen Instituten der Universität Frankfurt/Main (HAHN-WEINHEIMER) und Saarbrücken (ROST) ausgeführt. HAHN-WEINHEIMER übernahm dabei die analytischen Bestimmungen und den erzmikroskopischen Awaruit-Nachweis. Der Deutschen Forschungsgemeinschaft sei für finanzielle Hilfe zur Durchführung der Untersuchungen gedankt.

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The dissolution of silica from diatom walls*

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Abstract—Silica walls of diatoms, prepared by digesting cultured cells with nitric acid, dissolved more rapidly in media of higher pH or at higher temperatures. Most of the studies reported here were carried out in Tris buffer at pH 9.0–9.3 and at 19°C. The rate of dissolution under these conditions was slightly less than in sea water at pH 8.0, since NaCl accelerates the dissolution of silica. The silica from cleaned diatom walls dissolved in Tris buffer until, after 3–4 weeks, the solution had become saturated at 40–50 mg Si/l. (85–110 mg SiO₂/l.). The rate of solution decreased with time, probably due to the presence of silica in different states of hydration. Living cells suspended in buffer in darkness remained viable for many weeks during which time very little silicon dissolved from their walls. However, every treatment which killed the cells (heat, protein-denaturing agents, organic solvents, breakage) resulted in an increase in the rate of silica dissolution, although this rate was never as great as from acid-cleaned walls.

Experiments with EDTA indicated that a cationic inorganic factor was retarding silica dissolution from killed cells. Pretreatment of cleaned silica walls with salts of Al, Be, Fe, Ga, Gd, Se, Ti, Y and Yb at pH values between 2.0 and 9.0, and with Mn at pH values between 4.0 and 11.0, had various effects on the subsequent rate of dissolution of the silica at pH 9.0. At certain pH values each of these elements can evidently combine superficially with amorphous silica and thereby retard its rate of dissolution. Pretreatment of cleaned silica walls with salts of La, Mo, Cr, at pH values between 2.0 and 9.0, and with Ca and Mg at pH values between 4.0 and 11.0, had no effect on their subsequent dissolution at pH 9.0. Al, Be, Fe, Ga, Gd and Y were all capable of combining with silica walls at pH 8.0, which is the pH of sea water, and thereby retarding their subsequent dissolution. A single determination showed that the walls adsorbed Al equivalent to 1 per cent of their weight. In retarding dissolution of the silica, Al was as effective on killed, but intact, cells as on acid-cleaned walls.

The silica of nine samples of untreated diatomaceous earth of fresh-water and marine origins, ranging in age from Upper Cretaceous through Pliocene, was essentially insoluble under these conditions. Digestion in strong nitric acid freed only a small fraction of the silica for dissolution. The factor which retarded the initial dissolution of silica from natural marine phytoplankton could be removed completely by pretreating the cells with a chelation mixture of EDTA and oxalate. DHEG, which is reported to complex certain cations such as Fe, but to have no effect on Ca or Mg, was equally effective.

It can be concluded that certain adsorbed inorganic cations decrease the rate of dissolution of diatomaceous silica. In living diatom cells there may be an additional mechanism for stabilizing silica walls.

INTRODUCTION

NATURAL waters, both fresh and marine, are generally far from saturated with respect to silicic acid, i.e. more could be dissolved than is normally present in solution (COOPER, 1952; BRUEVICH, 1953; and KRAUSKOPF, 1956). The equilibrium in nature would therefore be in the direction of silica dissolution.

The amorphous silica structures in diatoms, radiolarians, sponges and silicoflagellates have been deposited by vital activity, and appear to be prevented from dissolving in their aqueous habitat while intact and associated with the living organisms. Under certain conditions, the siliceous structures remaining after the death of such organisms also appear to be resistant to solution, since silica deposits of biological origin are sometimes found in vast quantity in both fresh-water and

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marine environments (see CONGER, 1942; BRAMLETTE, 1946; and RIEDEL, 1959). COOPER (1952) has postulated that the surfaces of the siliceous skeletons may be protected against solution by some sort of an organic skin, possibly only a few molecules in thickness. ILER (1955) has likewise speculated that: (a) the magnesium, iron, aluminium, or other polyvalent cations in natural waters may produce a coating of insoluble silicates and thus prevent the enclosed silica from dissolving; or alternatively (b) organic complexes on the surface of the silica may prevent dissolution.

The present paper deals with studies on dissolution of the silica frustules of diatoms, in an attempt to adduce evidence for the presence of such a protective coating and to investigate its nature. In particular, the relative effects of various inorganic cations as protective agents have been studied. In principle, the method consisted of pretreating living or killed cells, or cleaned frustules, in various ways, and then allowing them to dissolve under controlled conditions over a period of days. The rate of solution was determined by sampling at intervals, removing the cells by centrifugation, and determining colorimetrically the silica in the supernatant solution.

MATERIALS AND METHODS

In order to obtain a supply of silica walls of uniform size and known composition, cells of *Navicula pelliculosa* (Bréb.) Hilse were grown in an inorganic medium containing (g/l.): K_2HPO_4 , 0.2; $MgSO_4 \cdot 7H_2O$, 0.2; $Ca(NO_3)_2 \cdot 4H_2O$, 1.0, dissolved in glass-distilled water. Trace elements were added as follows: 0.1 p.p.m. each B, Co, Cu, Mn, Mo; 0.3 p.p.m. Zn; 0.5 p.p.m. Fe. Silicate was added as $Na_2SiO_3 \cdot 9H_2O$ to give a soluble silicon concentration of 10 p.p.m.

Two-litre Pyrex Erlenmeyer flasks containing 1.5 l. of medium were sterilized by autoclaving and inoculated under sterile conditions. The cultures were constantly aerated by filtered air and illuminated at 3000 lux, at 20°C for 10 days. At the end of the growth period, the cells were allowed to settle and were concentrated to approximately 40 ml by decanting and removal of the supernatant medium. The cells harvested from 1.5 l. of culture provided sufficient siliceous frustules for one experimental run. The pH of the suspension was adjusted to 2.5–3.0 to dissolve precipitated phosphates, and the cells were immediately washed by repeated centrifuging and resuspending in distilled water. They were then concentrated to a suitable volume, and dispensed into small test tubes, 2 ml of cell suspension per tube, to give the same concentration of diatom silica in each tube of a given experiment. This varied between 2 and 3 mg SiO_2 from one experiment to another.

When "cleaned" frustules were required, 2 ml concentrated nitric acid were added to each tube and the mixture heated at 100°C for 15 min to decompose the organic matter. The frustules were freed from the acid by diluting with water and centrifuging, followed by three washings with distilled water.

In each experiment the cells or frustules in the small test tubes were first subjected to various pretreatments, with suitable control samples retained as required. The chemical agents used were removed by washing. The final cell or frustule preparation was suspended in 20 ml of 0.01 M Tris buffer, at pH 9.0–9.3, in polyethylene bottles (125 ml). Polyethylene centre wells containing 10% KOH were inserted into the containers to remove atmospheric CO_2 and thereby to aid in maintaining the pH of the suspension throughout the experimental period. The polyethylene bottles were then capped and stored at 20°C. When sea water was employed as the dissolving medium, centre wells were not used.

Although it would have been desirable to shake the suspensions during the time while the walls were dissolving, this was not feasible because of the large number of bottles involved and because of the presence of the centre wells containing KOH. All bottles were therefore left at rest during the dissolution period.

In order to follow the dissolution of the silica, samples were removed at intervals and the

soluble silicic acid appearing in the medium was determined colorimetrically by the use of ammonium molybdate and hydroquinone (LEWIN, 1954).

Soluble salts of the various elements tested were prepared in the following ways: aluminium metal powder, iron wire, gallium metal, Sc_2O_3 , Yb_2O_3 , Y_2O_3 or Gd_2O_3 dissolved in hot concentrated hydrochloric acid; TiO_2 dissolved in concentrated sulphuric acid; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, La acetate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, $\text{Cr}_2\text{K}_2(\text{SO}_4)_4$, $\text{Be}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ dissolved directly in the acetate-Tris buffer. Tris (hydroxymethyl) amino-methane buffer was obtained from the Sigma Chemical Company. EDTA or Versene (disodium salt of ethylenediaminetetra-acetic acid) and DHEG or Versene Fe-3 Specific (N:N'-di(2-hydroxyethyl) glycine) were obtained from Versenes, Incorporated, Framingham, Mass.

RESULTS

1. Preliminary

(a) *Effect of pH.* In preliminary experiments, acid-cleaned silica walls were suspended in Tris buffer (0.01 M) adjusted with HCl to pH 3, 6, 7, 8 and 9, and kept at 20°C. In media of higher pH, the silica frustules dissolved more rapidly (Fig. 1). Similar observations were made by JØRGENSEN (1955a, 1957). The rate at pH 9 was found to be most convenient for sampling purposes, and 0.01 M Tris buffer adjusted to pH 9.0–9.3 was employed in screw-capped polyethylene bottles for most of the experiments reported in this paper. By the use of centre wells containing KOH (see Methods) the pH was maintained at a constant level for many weeks (or it decreased in some cases to pH 8.6 if the bottles were opened several times). In those cases where sea water at pH 8 was employed for dissolution of the silica walls, no KOH-containing tube was inserted since it was found to cause the pH of the sea water to rise to pH 9.

(b) *Effect of temperature.* In preliminary experiments, silica walls were suspended in 0.01 M Tris buffer and kept at different temperatures. The rates of dissolution at 10°C, 15°C, 21°C, and 35°C are shown in Fig. 2. For the following experiments reported in this paper, the polyethylene containers were stored in a dark cupboard at about 19°C.

(c) *The rate of dissolution of silica walls in Tris buffer compared with that of sea water.* Silica walls dissolved more rapidly in sea water (pH 8.0) than in Tris buffer adjusted to the same pH (see Fig. 3). The lower rate in Tris buffer was not due to an inhibitory effect of the buffer, since walls dissolved in sea water *plus* Tris at the same rate as in sea water alone. The accelerated dissolution in sea water is attributable to NaCl (DIÉNERT and WANDENBULCKE, 1923). Silica walls in 2.5% NaCl and Tris at pH 8.2 dissolved at the same rate as in sea water (Fig. 3). Fluoride at concentrations of 1, 10 and 100 p.p.m. in Tris buffer at pH 8.0 was found to have no appreciable effect on the rate of dissolution of silica walls.

(d) *Removal of organic matter.* For the microscopic examination of diatom walls it is customary to "clean" the frustules, i.e. to free them of organic matter, by heating them with concentrated nitric acid. There was some question that the use of such strong acid might dehydrate or change the structure of the silica in the walls, thereby altering its subsequent dissolution. However, it was found that walls cleaned by heating at 100°C with 10% (by volume) nitric acid for 15 min dissolved in buffer at exactly the same rate as those cleaned with the concentrated acid. Lower concentrations were ineffective in destroying all organic cellular material.

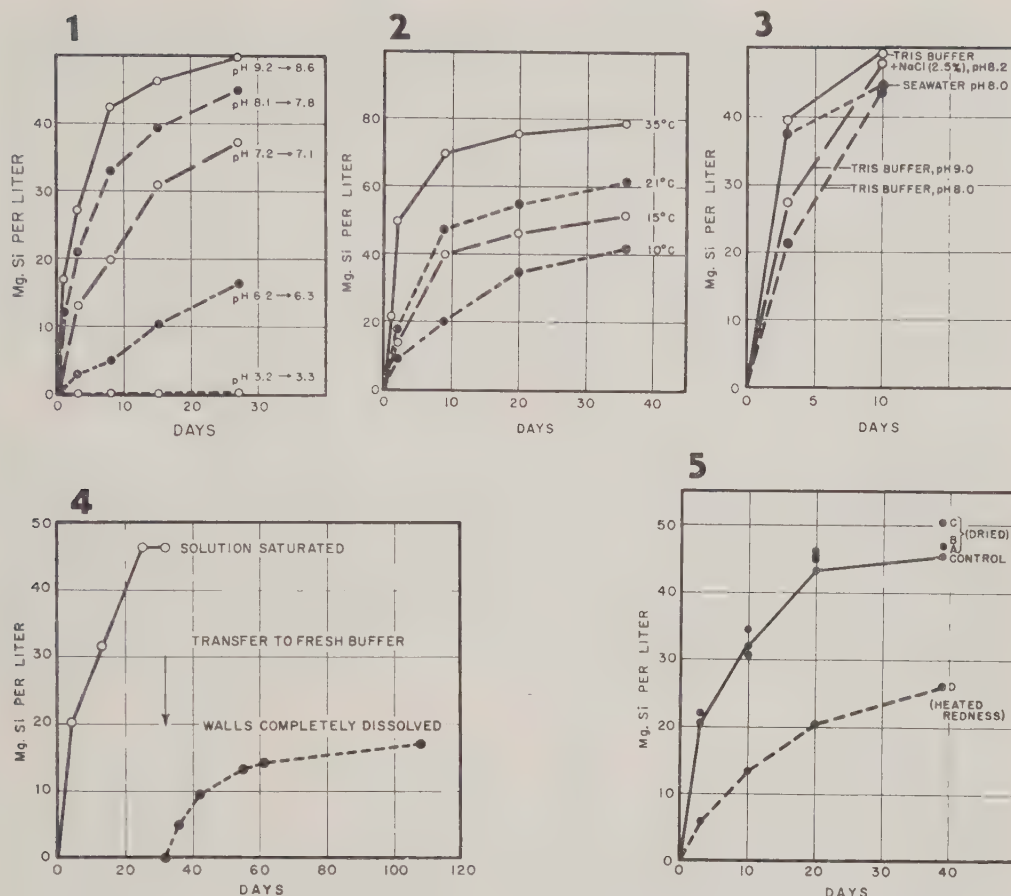


Fig. 1. Dissolution of silica from acid-cleaned valves at 19°C in 0.01 M Tris buffer, initial pH adjusted with HCl, final pH also shown.

Fig. 2. Dissolution of silica from acid-cleaned valves in 0.01 M Tris buffer, pH 9.0-9.3, at 10, 15, 21 and 35°C.

Fig. 3. Dissolution of silica from acid-cleaned valves in Tris buffer, in sea water, and in Tris buffer + NaCl, at 19°C.

Fig. 4. Dissolution of silica from acid-cleaned valves in 0.01 M Tris buffer, pH 9.0-9.3, at 19°C, showing decrease in rate with time.

Fig. 5. Dissolution of silica in 0.01 M Tris buffer, pH 9.0-9.3, at 19°C, from acid-cleaned valves: (a) dried in air, (b) dried in air and then in a vacuum desiccator over H_2SO_4 for 20 hr, (c) dried at 45°C for 23 hours, and (d) heated to redness for 3 min in a platinum crucible. Control valves not dried.

(e) *Change of solution rate with time.* The number of silica walls employed in each experiment was usually in excess of that required to saturate the medium with dissolved silicic acid. In most experiments the levelling of the dissolution curve between 40 and 50 mg Si/l. was therefore due to the attainment of the solubility equilibrium rather than to the complete dissolution of all the silica from the walls. To illustrate this, in one experiment the silica walls remaining after equilibrium had been reached were collected by centrifugation, resuspended in fresh buffer, and made up to the same volume as before. Silica from the walls then continued to pass into

solution until they completely dissolved (see Fig. 4). From the shape of the curve it is apparent that the rate of solution of the silica in water decreases with time (JØRGENSEN, 1955a, 1957), presumably indicating the existence of silica in different states of hydration.

(f) *Dissolution of silica from dried silica walls.* In the experiments reported in this paper the silica walls were never allowed to dry. Since for some purposes it might be convenient to work with material stored in the dry state, a comparison was made of the rates of dissolution of silica from walls, (a) dried in air, (b) dried in air and then in a vacuum desiccator over H_2SO_4 for 20 hr, (c) dried at 45°C for 23 hr and (d) heated to redness for 3 min in a platinum crucible. It was found that preparations (a), (b) and (c) dissolved at the same rate as wet walls, whereas the rate of dissolution of (d) was appreciably reduced (Fig. 5).

2. *Dissolution of silica from intact cells and from cleaned frustules*

When living cells were suspended in Tris buffer at pH 9.0 in darkness, silica went into solution only very slowly, and reached approximately 2 mg Si/l. after 50 days. After 30 days in the dark, suspensions streaked out on agar media and illuminated showed a high proportion of viable cells. The silica from heat-killed cells dissolved more rapidly, and reached 5–30 mg/l. in different experiments at the end of 50 days. Cleaned silica walls dissolved still more rapidly in Tris buffer at pH 9.0, until after 3–4 weeks the solution had reached saturation at 40–50 mg Si/l. (85–110 mg SiO_2 /l.) (Fig. 6).

3. *Experiments to determine whether the agent retarding dissolution is of organic nature*

Since the silica of the walls dissolved more rapidly after the cells had been digested with nitric acid, it was considered possible that some organic component of the whole cells might be protecting the silica walls from dissolving. The following experiments to test this hypothesis were carried out.

Cells were treated with the following protein-denaturing or -solubilizing agents: (1) 0.5% pepsin, pH 2.0, 30°C , for 14 hr; (2) 0.5% trypsin, pH 7.9, 30°C , for 24 hr; (3) 40% urea, pH 3.0, for 3 days; (4) a combination of enzyme and urea treatments; (5) 5% bile salts, pH 6.4, for 3 days. In another experiment, cells were extracted overnight with the following organic solvents: ethanol, acetone, diethyl ether, methanol:benzene (1:3), glacial acetic acid and pyridine. None of these treatments affected the subsequent rate of dissolution of the silica walls, which in all cases paralleled that of heat-killed cells.

The possibility was next considered that a protective coat might cover only the "outer" surface of the valves, and that, if the cells were broken open, the "inner" surfaces of the silica walls might become exposed to rapid dissolution. Cells were ruptured by first compressing them to 28,000 lb/in² in a pressure chamber (French pressure cell, manufactured by the American Instrument Co.), and then extruding them through a small orifice. Although some cells remained apparently intact after this treatment, none of them proved viable. Most were broken open, and free silica walls could be seen floating among cellular debris in the suspension. Nevertheless, their rate of dissolution was unchanged, again paralleling that of heat-killed cells.

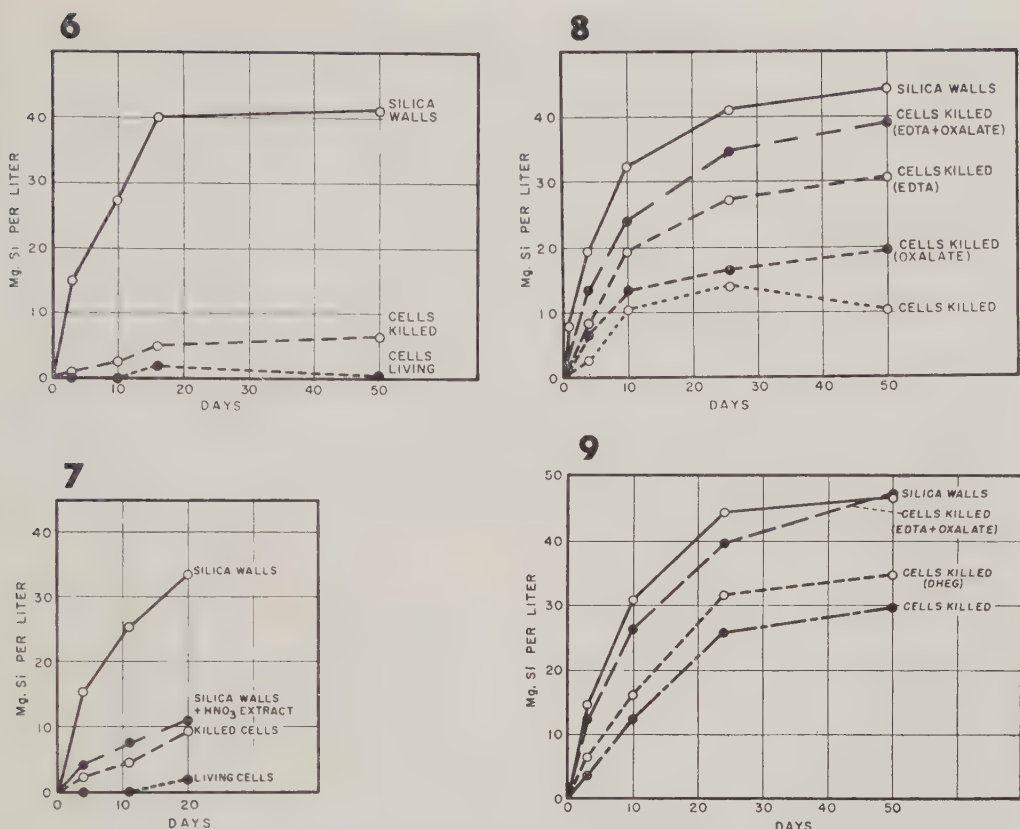


Fig. 6. Dissolution of silica in 0.01 M Tris buffer, pH 9.0-9.3, at 19°C, from whole cells (living and heat-killed), and from acid-cleaned valves.

Fig. 7. Dissolution of silica in 0.01 M Tris buffer, pH 9.0-9.3, at 19°C, from whole cells (living and heat-killed), from acid-cleaned valves, and from acid-cleaned valves subsequently treated with a nitric acid cell extract.

Fig. 8. Dissolution of silica in 0.01 M Tris buffer, pH 9.0-9.3, at 19°C, from silica valves, from heat-killed cells, and from heat-killed cells extracted with oxalate, EDTA, or EDTA + oxalate.

Fig. 9. Dissolution of silica in 0.01 M Tris buffer, pH 9.0-9.3, at 19°C, from silica valves, from heat-killed cells, and from heat-killed cells extracted with DHEG or with EDTA + oxalate.

It was concluded that whatever protective mechanism was responsible for retarding silica dissolution completely coated each valve of the frustule.

4. Experiments to determine whether the agent retarding dissolution is of inorganic nature

(a) *Tests with the nitric acid extract.* The nitric acid extract, obtained when the cells were cleaned, was evaporated to dryness, redissolved in water, and adjusted to pH 7.1 with NaOH. Cleaned silica walls, treated with this extract for 30 min and then thoroughly washed, subsequently dissolved at the same rate as heat-killed whole cells, i.e. considerably more slowly than the cleaned silica walls (see Fig. 7). Since all organic matter had presumably been destroyed by oxidation, this

experiment implicated an inorganic element or elements, which could be removed from the cells by treatment with nitric acid, and which could be reassociated with the silica walls to reduce their rate of dissolution.

(b) *Effect of treating heat-killed cells with chelating agents, etc.* Attempts were then made to remove the inorganic factor by some means other than digestion with nitric acid.

Widely differing ions, such as Fe and Ca, could probably be removed from silica walls by EDTA and oxalate. Another chelating agent, N:N'-di(2-hydroxyethyl) glycine (DHEG or "Versene Fe-3 Specific") is said to complex Fe, Cu, Ni, Co, and Mn, but not Ca or Mg (CHABEREK *et al.*, 1953). On the supposition that the factor was a polyvalent cation, cells were treated with EDTA, citrate, oxalate, EDTA *plus* citrate, EDTA *plus* oxalate and, in another experiment, with DHEG, all at 0.01 M adjusted to pH 6.8. They were then washed and suspended as usual in Tris buffer at pH 9.0. EDTA was more effective in accelerating the subsequent rate of dissolution of the silica than was either citrate or oxalate alone; EDTA *plus* citrate or oxalate was even more effective, although the rate of dissolution of the silica did not quite reach that of the acid-cleaned frustules (Fig. 8). DHEG was only slightly effective (Fig. 9).

5. *Rate of dissolution of cleaned silica walls after treatment with various ions*

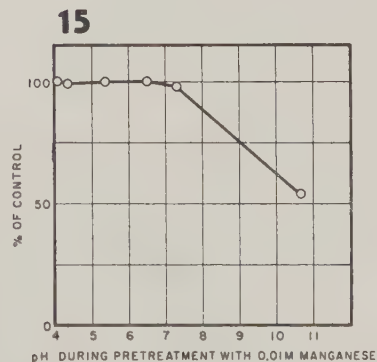
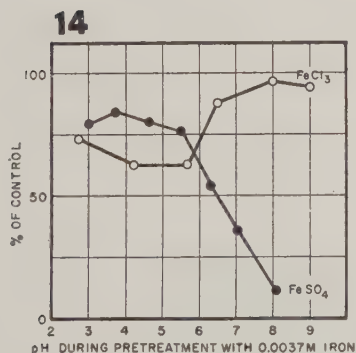
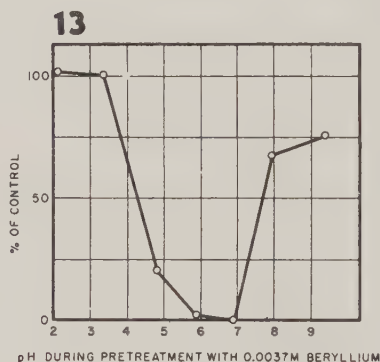
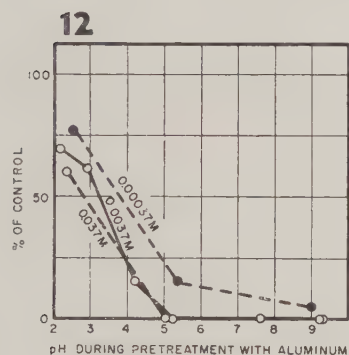
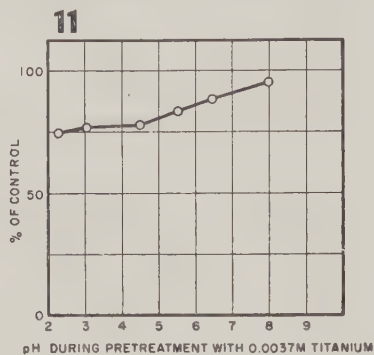
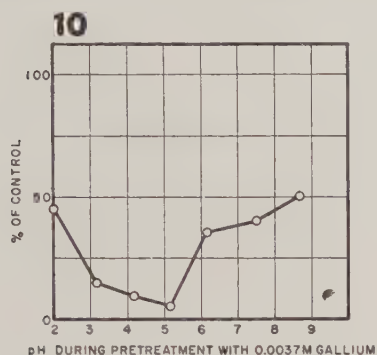
It thus appeared that some cations, for which EDTA has a chelation affinity, either retarded the dissolution of the silica or changed its solubility by coating the frustules. In order to determine what ions could have this effect, cleaned silica walls were treated for 3 hr with salts of the following metals: divalent Ca, Mg, and Mn; trivalent Al, Be, Cr, Fe, Ga, Gd, La, Sc, Y, Yb; Ti^{4+} and Mo^{6+} . The divalent ions were used at a concentration of 0.01 M at pH values between 4.0 and 11.0 in 0.1 M acetate *plus* 0.01 M Tris buffer. All other salts were used at a concentration of 0.0037 M in the same buffer adjusted to pH values between 2.0 and 9.0. In those cases where an insoluble precipitate formed, this was removed by centrifugation, and only the supernatant was used for treating the silica frustules. At the end of the 3-hr treatment period, the frustules were washed thoroughly and suspended in Tris buffer at pH 9.0–9.3. Treatment of the silica walls with the buffer mixture alone at various pH values had no effect on the subsequent rate of dissolution of the silica walls.

La, Mo, Cr, Ca and Mg pretreatments were without significant effect on the subsequent rate of dissolution of the silica walls. The other ions retarded the dissolution of the silica to various degrees as illustrated in Figs. 10–19.

Since the results obtained with Al at 0.0037 M were the most striking, Al was also tested at concentrations of 0.00037 M and 0.037 M, with similar results (see Fig. 12). Above pH 8.0, Al in solution is presumably present in appreciable amounts as aluminate ion (HUTCHINSON, 1957), which in these experiments appeared to be as effective as the Al^{3+} ion in retarding the dissolution of the silica walls.

Freshly prepared $FeCl_3$ was only effective below pH 6, since above this pH all the Fe^{3+} ion had evidently been precipitated as $Fe(OH)_3$ before addition of the supernatant to the silica walls. Freshly prepared $FeSO_4 \cdot 7H_2O$ was most effective between pH 6 and pH 8.5, apparently due to slow atmospheric oxidation of the ferrous ion to the ferric state. At those pH values where Fe was effective, the silica walls

assumed a rusty colour, which was not removed by washing. Above pH 8.5 neither source of Fe ions was effective in preventing the subsequent dissolution of silica walls. In an attempt to render the adsorption of iron more effective, an acid solution of FeCl_3 was added to a suspension of silica walls in acetate-Tris buffer. The final Fe concentration was 0.004 M and the pH was brought up to 5.2. After 3 hr in this medium, the cells were washed and resuspended in Tris buffer at pH 9. This pretreatment had no appreciable effect in decreasing the rate of dissolution of



Figs. 10-19. Silica in solution (per cent of the control) at the end of 10 days in Tris buffer, pH 9.0-9.3, at 19°C, plotted against the pH values at which acid-cleaned silica valves were pretreated for 3 hr with solutions of metal salts as indicated.

silica walls beyond that shown for FeCl_3 in Fig. 14. After 10 days the amount of silica which had gone into solution was 56 per cent of the control.

Aluminium, beryllium, gadolinium, gallium, iron and yttrium were of especial interest in that they were able to react with silica walls in the range of pH 8.0, which is the pH of sea water.

6. *A quantitative determination of Al combined with silica*

It is logical to assume that the reaction involved an adsorption of these cations on the cleaned silica surfaces. In order to test this assumption the following experiment with Al was carried out.

A known amount of acid-cleaned valves of *Navicula pelliculosa* was treated with a large excess of a clear solution of 0.0037 M Al in acetate-Tris buffer at pH 5.25 for 17 hr. At the end of this time the valves were thoroughly washed, and a quantitative analysis for adsorbed Al was carried out on the valves by D. P. KHARKAR, Scripps Institution of Oceanography, La Jolla, California, employing a micromethod devised by W. SACKETT. It was found that 5.5 mg of silica valves had adsorbed 57.4 μg of Al, equivalent to 1.04 per cent by weight.

7. *Rate of dissolution of silica from intact cells after pretreatment with aluminium*

Since Al ions could combine with cleaned silica walls at various pH values and retard their subsequent rate of dissolution in Tris buffer at pH 9.0, it was of interest to determine whether the silica surfaces of intact diatom cells were likewise available for combination with Al. Cells were first killed and treated for 10 min with EDTA plus oxalate (0.01 M, pH 7.3) to remove inorganic protective agents from the cell surfaces (as in Fig. 8).

After washing, such cells were treated with 0.0037 M AlCl_3 in buffer adjusted to various pH values. After 3 hr, the cells were again washed, and then transferred to Tris buffer at pH 9.0. The results after 10 days showed that treatment with EDTA plus oxalate had increased the subsequent rate of dissolution of the silica beyond that of heat-killed cells (as in Fig. 8). However, from those killed cells which had then been pretreated with Al, the silica dissolved at a greatly decreased rate (see Fig. 20). This indicated that Al could combine with the silica surfaces of intact cells, just as it could with cleaned silica walls, thereby retarding their subsequent rate of dissolution. Cleaned walls and intact cells differed in the extent to which the Al combined with silica walls at various pH values (compare Fig. 20 with Fig. 12).

8. *Dissolution of silica from fossil diatom walls*

Since such ions as Fe and Al may retard the rate of dissolution of silica walls, it was of interest to determine to what extent such metal ions might be responsible for the relative insolubility of fossil diatom walls.

Nine samples of diatomaceous earth, fresh-water and marine, ranging in age from Upper Cretaceous through Pliocene, were examined. The material was first powdered by grinding in a mortar and 5 mg samples of each earth were leached in 20 ml of Tris buffer at pH 9.3. In each case, after 35 days only a small amount of soluble silicon had appeared in the medium (approximately 1 mg Si/l. Similar samples first extracted with hot concentrated nitric acid before being placed in the Tris buffer gave off more soluble silicon to the medium than did the untreated walls, ranging

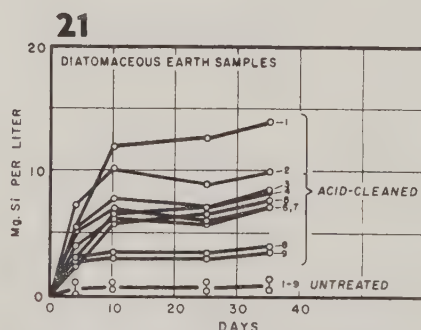
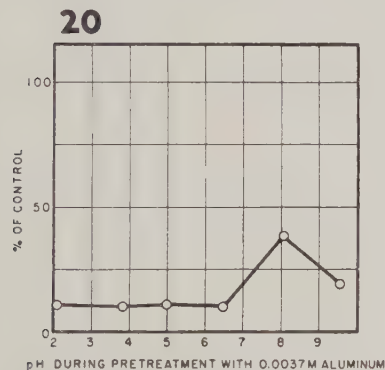
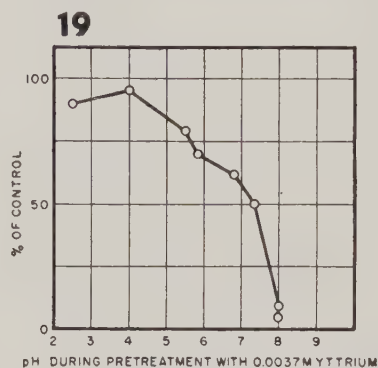
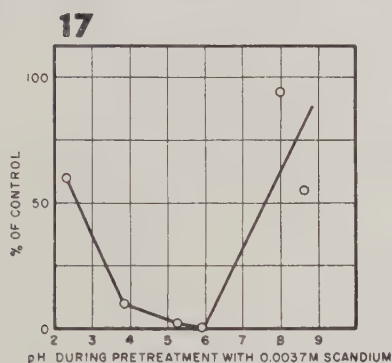
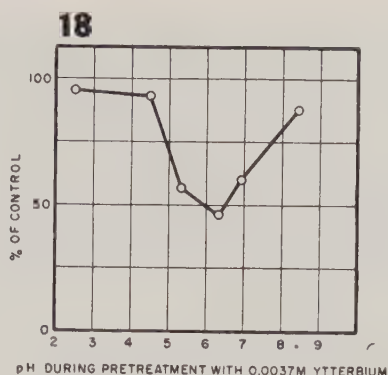
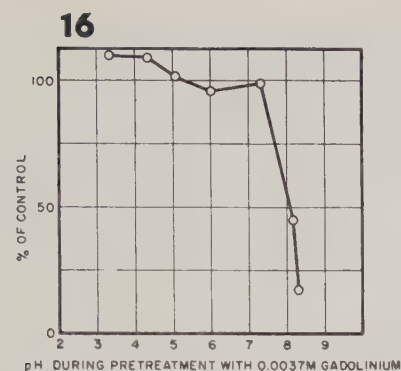


Fig. 20. Silicon in solution (per cent of the control) at the end of 10 days in Tris buffer, pH 9.0-9.3, at 19°C, plotted against the pH values at which whole heat-killed cells were pretreated with solutions of AlCl_3 .

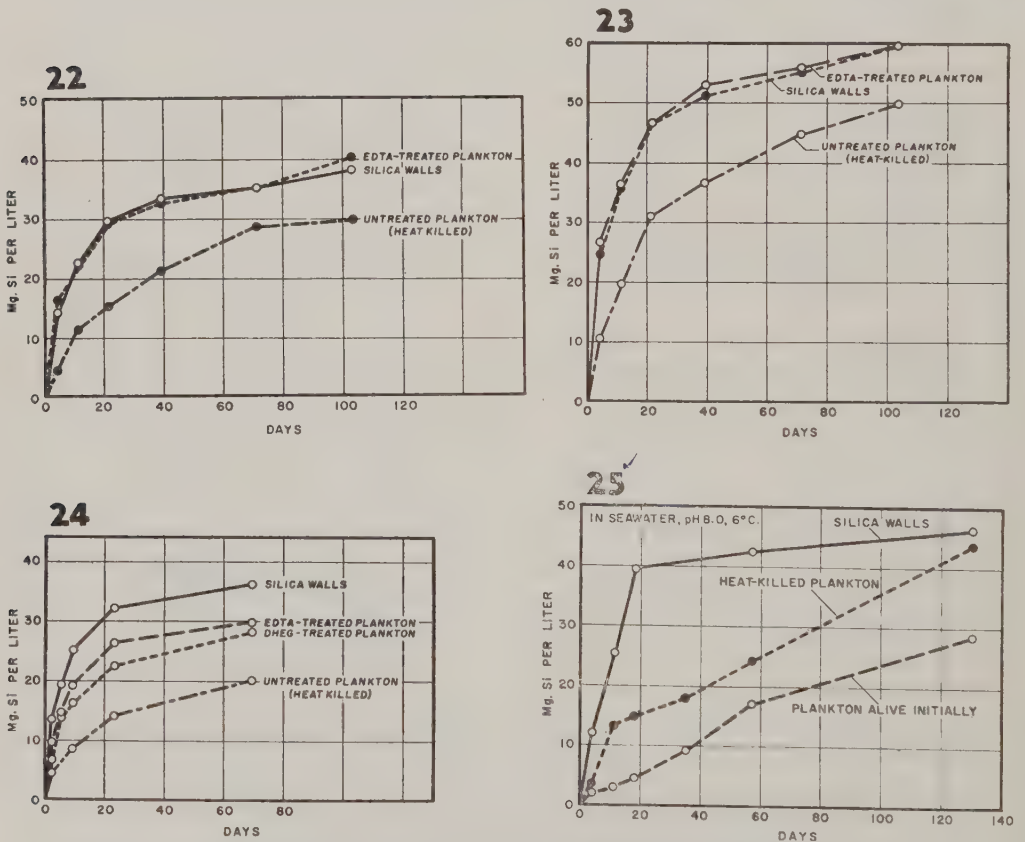
Fig. 21. Dissolution of silica in Tris buffer, pH 9.0-9.3, at 19°C, from diatomaceous earths, untreated and acid-cleaned.

- (1) Terrebonne, Ore., 100,000-200,000 years (fresh-water).
- (2) Sierra Vista Hill, Los Angeles, Calif., Upper Miocene.
- (3) Shark Tooth Hill, Kern Co., Calif., Middle Miocene.
- (4) Chico Martinez Creek, Kern Co., Calif., Upper Miocene.
- (5) Walteria, Calif., Upper Miocene.
- (6) Maria Madre, Mexico, Upper Miocene.
- (7) Hat Creek Crossing, Shasta Co., Calif., Pliocene.
- (8) Panoche Hills, Fresno Co., Calif., Upper Cretaceous
- (9) Pit River, Calif., Pliocene (fresh-water).

from 3 to 13 mg Si/l. (Fig. 21). Since each sample contained considerably more silica than that required to saturate the solution, nitric acid treatment had served to free only a fraction of the silica for dissolution. The reduced solubility of silica from fossil diatom walls may be due to changes in microstructure of the silica with the passage of time. It is significant that the whitest sample (a fresh-water Pliocene diatomite from Pit River, California), which by X-ray diffraction showed no evidence of crystalline impurity even after preliminary acid digestion, showed only a low rate of dissolution in aqueous buffer, yielding in solution 3.5 p.p.m. Si after 35 days.

9. Dissolution of silica from natural phytoplankton

Phytoplankton consisting almost exclusively of diatoms (species of *Skeletonema*, *Chaetoceros* and *Rhizosolenia*) was collected with a No. 20 net from a wharf in Woods



Hole in January 1959. Aliquots of the sample at two dilutions ($\times 1$, $\times \frac{1}{2}$) were (a) killed by immersion for 5 min in a boiling water bath, (b) killed and then extracted with a mixture of EDTA (0.01 M), oxalate (0.01 M) and Tris buffer (0.01 M) at pH 6.8, and (c) digested with hot concentrated nitric acid to destroy organic matter. The samples were then washed, and suspended in 20 ml Tris buffer (0.01 M) at pH 9.0 in polyethylene containers. At intervals over a period of 104 days, samples were removed, centrifuged, and the dissolved silicon in the supernatant determined.

The silica from plankton cells pretreated with EDTA *plus* oxalate dissolved at the same rate as that from acid-cleaned walls. On the other hand, the silica from killed, though otherwise untreated, plankton dissolved more slowly, initially at about half the rate of the cleaned walls. The greater part of the silica had dissolved from the EDTA-treated cells and the acid-cleaned walls after 30 days, but from the killed plankton only after 100 days (Figs. 22 and 23).

Another sample, from 70 miles offshore, consisting of an entirely different complement of diatoms (predominantly *Thalassionema nitzschioides* and *Coscinodiscus* sp.) was treated in a series similar to the previous sample, and exactly the same relationships were obtained. When pretreated with DHEG (0.01 M, in Tris buffer, pH 6.8), the silica from the diatom cells dissolved at the same rate as from cells pretreated with EDTA (Fig. 24).

Apparently some factor, presumably cations originally combined with the silica but removable by EDTA, DHEG or nitric acid, was instrumental in reducing the rate of dissolution of the silica from killed plankton.

The above experiments with naturally occurring phytoplankton were carried out in Tris buffer at pH 9.0 at 20°C. In order to approach more closely to natural conditions, another phytoplankton sample was set up in sea water, pH 8.0, at 6°C. Untreated cells, which were living at the outset, were also included for comparison. Glass flasks were used in this case, since commercial polyethylene vessels liberate some toxic substance into the medium. Nevertheless, such cells did not survive more than a few days, since the suspension was dense and was maintained in the dark to preclude photosynthesis. Correspondingly, during the first few days, silica dissolved more slowly from these untreated cells than from samples killed by heat, whereas later the rates of the two samples were similar (Fig. 25).

DISCUSSION

Living cells of fresh-water diatoms, grown in the laboratory and stored in darkness at pH 9.0 in a medium containing neither organic substrate nor nutrient salts, remained for the most part viable for several weeks. They released silicon into the medium at a much lower rate than cells which were initially dead. This difference could be attributed either to a vital suppression of the dissolution of the walls, or to the ability of the living cells to reabsorb silicic acid from the medium almost as fast as the silica dissolved. The latter possibility seems unlikely, since the uptake of soluble silicate by diatoms is a process requiring energy (LEWIN, 1955), whereas the cells used in these experiments were under starvation conditions and had no source of energy other than the respiration of depleted endogenous reserves. More probably, the silica in the walls of living cells was protected by some physico-chemical system, which was disrupted as soon as they died.

Every treatment which killed the cells (heat, protein-denaturing agents, organic solvents, breakage) gave the same result, i.e. an increase in the rate of dissolution of the silica walls. However, this rate could be further accelerated by treatment with a chelating agent such as EDTA, which presumably removed a cationic inorganic factor retarding silica dissolution. Since iron was present in the original growth medium, this was probably the element concerned.

Aluminium is one of the most effective elements in combining with silica and thereby reducing its solubility and retarding its rate of dissolution (JEPHCOTT and JOHNSTON, 1950; GODBERT and HALPIN, 1955; GOTO, 1956; and OKAMOTO *et al.*, 1957). The hydrated Al^{3+} cation presumably reacts with free hydroxyl groups at the silica surface. ILER (1955, pp. 68–69) discussed in general terms the precipitation of polysilicic acid from solution by the addition of salts of various metals. Though the polysilicic acid of diatom walls is not in colloidal solution, similar chemical combinations would presumably occur at the surface in the presence of metal ions. The evidence indicates that "Combination with silicic acid does not occur much below the pH at which the metal hydroxide would be formed (either as a sol or as a precipitate) on prolonged standing." ILER suggested that the reaction could be considered as a combination between a silanol group ($\cdot\text{SiOH}$) and a basic metal ion (such as $\text{Fe}(\text{OH})^{2+}$).

The results obtained in the present study indicate that certain metal ions under specific conditions may combine with the silica walls of diatoms and affect either their subsequent rate of dissolution or their final solubility. There is no direct information on the role of such combinations in nature. It should further be pointed out that the concentrations of cations employed for treatment of the silica walls in the experiments reported here were mostly in excess of those normally present dissolved in sea water. For instance, SIMONS *et al.* (1953) found that the soluble Al in sea water averaged 0.0025 mg/l. (approx. 10^{-7} M) and the soluble Fe averaged 0.0026 mg/l. (approx. 5×10^{-8} M), concentrations considerably below those employed here.

The amounts of Al, Be, Fe, Ga, Gd and Y, in sea water are too small to have any direct effect on the rate of dissolution of amorphous silica and, when cleaned walls of diatoms are suspended in sea water, the silica goes into solution. However, it is possible that, if the silica valves while a part of the intact living cell could be initially protected against solution by some other biophysical or biochemical means, there would be time later for colloidal ferric and aluminium hydroxides to be passively adsorbed and accumulated on the new surfaces and the system to be thereby stabilized. Observations on the adsorption of ferric hydroxide on diatom surfaces have been published by HARVEY (1937a), GOLDBERG* (1952), GEISSLER (1958) and IVES (1959). It might be mentioned in this connexion that the true age of a diatom valve is not necessarily that of the cell which bears it, since, by the unique nature of diatom cell division, each daughter cell inherits one of the parental silica valves, which may already have been transmitted in this way for several generations. ROGALL (1939) analysed the walls of marine planktonic diatoms and found iron or

* GOLDBERG, in personal discussion, agreed that the high values published in his 1952 paper for the iron content of diatoms could be explained by a passive adsorption of particulate or colloidal iron upon the surfaces of the diatom cell, independent of the living activity of the cell. His use of the term "assimilation" was unfortunately misleading.

aluminium oxides making up approximately 1.5 per cent of the ash weight. SPOONER (1949) showed that nearly all of the radioactive yttrium taken up by living or dead cells of a diatom (referred to simply as "Nitzschia") was adsorbed on the surface of the walls.

Investigations of the rates of dissolution of amorphous silica in water and of its solubility, i.e. equilibrium concentration under various conditions (ALEXANDER *et al.*, 1954; ILER 1955; KRAUSKOPF, 1956, 1959; WHITE *et al.*, 1956; GREENBERG, 1957; OKAMOTO *et al.*, 1957; SIEVER, 1957) indicate in some cases marked differences between the forms of amorphous silica, i.e. colloidal silica, silica gel, opal and silica glass. These observations, reviewed by KRAUSKOPF (1959), are of interest in relation to the differences in solubility between the amorphous silica from Recent (i.e. contemporary) diatoms and that from fossil diatoms. Recent diatom silica dissolves readily, at a rate similar to that of silica gel, whereas fossil diatomite dissolves very slowly. According to KRAUSKOPF (1959), WHITE has obtained values of 22 p.p.m. SiO_2 in fresh water and 34 p.p.m. SiO_2 in sea water in which diatomite has been dissolving for a period of 2 years. These values are in the same range as those reported here for diatomaceous earths which had been dissolving for 35 days, but in this case the material had first been cleaned with nitric acid to remove protective ions. One may ask what changes in the structure or chemical nature of the silica can have taken place to account for the differences in behaviour between Recent and fossil material. Measurements of the specific surface area (by the nitrogen adsorption method) of walls of the fresh-water species, *Navicula pelliculosa*, and of the marine species, *Coscinodiscus asteromphalus*, each grown in culture, gave values of 123 m^2/g and 89 m^2/g , respectively (LEWIN, unpublished). The average specific surface area of fossil diatomaceous earth was reported to be 22 m^2/g (ILER, 1955). These values indicate a reduction of specific surface area on ageing. Since the rate of solution (GREENBERG, 1957; GOTO, 1958) and the final solubility depend on the "available surface," i.e. the free silanol (SiOH) groups of the silica polymer (ALEXANDER, 1957), any loss of surface would be expected to result in a lower rate of solution.

The physical and chemical reactions involved in the fossilization of diatom walls, and the length of time required for the process, are unknown. ROGALL (1939) found that Recent, post-glacial, and interglacial diatom deposits, examined by X-ray diffraction methods, showed only amorphous structure, whereas in geologically older material he obtained some evidence for crystallinity. SWINEFORD and FRANKS (1959) published X-ray diffraction diagrams of a fossil diatomaceous marl showing that the diffraction pattern was distinctly different from the disordered low-cristobalite diagrams given by other forms of opal. The formation of diatom-type opal is thought to be a direct consequence of the chemical purity of the silica and the lack of cations necessary for the formation of a low-cristobalite structure disordered by incorporated tridymite. GEISSLER (1958) found that the walls of Recent diatom adsorbed dyes to the same degree as silica gel, whereas fossil walls were less reactive, being less strongly charged than Recent material.

Sporadic observations have been made on the dissolution of diatomaceous silica, some on recent cell material (KING and DAVIDSON, 1933; ATKINS, 1945; JØRGENSEN, 1955a, 1957; GOLTERMAN, 1960) and some on diatomaceous earths

(JEPHCOTT and JOHNSON, 1950; KRAUSKOPF, 1956; HOSS 1959). Since the silica of Recent diatoms differs from that of fossil materials, one would expect older samples to exhibit progressive degrees of fossilization, and thus different solubilities. The solvents, pH and temperatures employed in these studies were dissimilar, and therefore little can be gained from a comparison of the results.

The thickness of diatom walls varies considerably between species, in cells of different ages and conditions (LUND, 1950; JØRGENSEN, 1955b, 1957; LEWIN, 1957). For example, walls of *Coscinodiscus asteromphalus* may reach 25,000 Å in thickness whereas those of *Navicula pelliculosa* may range in average thickness from 200 Å to 600 Å (LEWIN, 1957). Obviously such variation in the average surface/volume ratio, as well as in the pattern of thickening and of microscopic pores, has a profound influence on the rate of solubility of the silica, as it may also have on the rate of fossilization. In many cases it has been observed that the specific composition of diatom skeletons in bottom deposits fails to reflect that of the living phytoplankton, apparently because the more delicate species tend to be eliminated and only the more resistant walls persist (HART, 1934, 1942; KOLBE, 1957). There may in addition be invisible differences in the submicroscopic constitution of the walls and in the distribution of the more soluble silanol groups. And we must now recognize the importance of adsorbed cations, such as Fe and Al, and perhaps also of organic protective coatings, in depressing the rate of solution of diatom walls. Nothing is known of the various conditions in the digestive tracts of diatom-eating planktonic animals and their predators which may have an appreciable influence on the degree of comminution and the rate of solution of silica walls. For all these reasons, no general statement of their solubility under natural conditions can be made. We cannot readily assess the factors involved in determining which skeletons of planktonic diatoms will dissolve, and which will persist to accumulate in bottom deposits, there to give rise to a diatomaceous ooze and, eventually, a diatomite.

Furthermore, those silica walls which persist long enough to reach the sediment, either associated with living cells or as empty frustules, are then subjected to a new set of physical and chemical factors peculiar to the particular sediment in question. For instance, ARRHENIUS (1952) observed that skeletons of diatoms and radiolarians were well preserved when associated with calcareous deposits in the Equatorial Pacific sediments and in several clays from the Central Pacific, whereas the siliceous structures associated with pelagic clays of the East Pacific were markedly corroded. RIEDEL (1959) pointed out that in areas of rapid sedimentation most siliceous skeletons are well preserved, whereas in areas of slow sedimentation many show partial dissolution. In the interstitial waters of some bottom sediments which may be already saturated with soluble silicic acid (BRUEVICH, 1953), as for example in beds of volcanic ash (see BRAMLETTE, 1946), the diatom frustules would tend to remain undissolved. OPPENHEIMER and KORNICKER (1958) described anaerobic marine sediments saturated with H_2S and CO_2 , with pH values of from 5.4 to 7.6; under such reducing conditions, Fe associated with the walls might be removed as FeS , and the silica might then be free to dissolve. Its solubility would also be influenced by the solubility equilibria established by the mineral composition of the solid phase in the sediment (BRUEVICH, 1953).

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Hydrology of tritium in the Ottawa Valley*

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Abstract—Tritium deposition in rainwater at Ottawa, Canada, is reported for the years 1953–1959. Correlation with the tritium content of drainage water in the district has allowed study of the hydrodynamics of the water system. A turnover rate constant of 0.27 year^{-1} has been found for a storage reservoir of 2.1 m. The fraction of fresh precipitation in re-evaporated water has been estimated as 0.55 ± 0.1 . A deposition rate of cosmic tritium of $1.3 \pm 0.1 \text{ atoms/cm}^2 \text{ sec}$ has been obtained from early data.

INTRODUCTION

THERMONUCLEAR tests have released large amounts of artificial tritium to the environment in recent years. While this has introduced major problems of contamination into studies of the equilibrium distribution of cosmic-ray tritium in the water systems of the world, e.g. for glaciological or oceanographic dating purposes, it has raised current natural tritium levels to a more easily measured range and facilitated studies of dynamic phenomena.

Measurements of tritium levels in natural waters during the past few years have been reported in papers by KAUFMAN and LIBBY (1954), VON BUTTLAR and LIBBY (1955), BROWN and GRUMMITT (1956), BEGEMANN and LIBBY (1957), GILETTI *et al.* (1958), VON BUTTLAR and WENDT (1958), and VON BUTTLAR (1959). Several of these authors have considered in some detail the hydrological implications of their data. CRAIG (1957a, b), BOLIN (1958), and ERIKSSON (1958) also have discussed many of the dynamic factors involved in the dispersal of tritium in nature and applied them to the data of LIBBY and co-workers.

This paper reports tritium deposit at Ottawa, Canada, for the period 1953–1959 and considers the hydrodynamics of its appearance in drainage waters of the district. A simplified model of the hydrologic system will be developed and tested by comparing its dynamic response with the observed fluctuations of tritium in river water resulting from injections of bomb tritium in rainwater during the past few years. The turnover rate, storage capacity and feed-back characteristics of the upper Ottawa drainage basin will be deduced on the basis of this model.

Physiography of the upper Ottawa drainage basin

As a result of the circuitous nature of the upper reaches of the Ottawa River, illustrated in Fig. 1, most of this watershed lies within 200 miles of Ottawa. It is believed that the average tritium deposit at Ottawa will be representative of that for several hundred miles around at least, and is considered to be a measure of tritium injection into the Ottawa drainage basin.

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THE OTTAWA DRAINAGE BASIN



Fig. 1. The Ottawa drainage basin.

- | | |
|---------------------|------------------------|
| (1) Ottawa. | (7) Mississippi R. |
| (2) Deep River. | (8) Madawaska R. |
| (3) Ottawa R. | (9) Bonnechere R. |
| (4) South Nation R. | (10) Petawawa R. |
| (5) Rideau R. | (11) Temiskaming. |
| (6) Gatineau R. | (12) Dozois Reservoir. |

----- Limits of Ottawa R. drainage basin above Deep River.

The concentration of tritium in river water will reflect its discharge from that portion of the drainage basin which lies upstream from the sampling site, in the present instance Deep River, Ontario. Location of this sampling point 6 miles upstream from the Atomic Energy of Canada Ltd. establishment at Chalk River avoided any possibility of contamination from this source.

The Ottawa River extends for a distance of 400 miles above Deep River and drains an area of 24,000 miles², all of which is within the Canadian Shield. The average discharge rate for this area over the period 1950–1959 was 28,260 ft³/sec. Monthly average discharge ranges between 13,000 and 50,000 ft³/sec but for 6 or 7 months of the year it is within ± 5000 ft³/sec of the yearly average rate.

The bedrock geology of the drainage basin above Deep River is one of Pre-Cambrian granites, gneiss and other crystalline and metamorphic rocks through which water moves in fractures and joints. There is extensive rock outcrop on all slopes, but the valleys are generally wide and well filled—frequently to depths of 100–200 ft—with glacial drift consisting of till, lake clays and river alluvium

providing considerable ground storage capacity. Numerous shallow elongated lakes in tributary valleys tend to be surrounded by peaty ground. Dams create a number of large surface reservoirs on the main stream in conjunction with hydroelectric development. Approximately 6-8 per cent of the area is water covered. Vegetation is that of the Boreal forest region—primarily coniferous but with a general admixture of white birch and poplar.

The foregoing indicates the extent of the basin and suggests its large water storage capacity. A conventional hydrological study involving analysis of local geology and permeability measurements, while yielding very detailed information, is a major undertaking for such a large area. On the other hand, correlation of the injection and discharge of tritium in such a drainage system should give information on the average turnover and storage characteristics of the system without extended measurements throughout the area. When the system has been thrown out of equilibrium by a transient increase in the injection rate, feedback of tritium to the atmosphere by evapotranspiration will be affected and may be subject to investigation by comparison with prior conditions.

ANALYTICAL TECHNIQUE

The detailed method used in this study has been described previously (BROWN and GRUMMITT, 1956) and involved enrichment of the heavy isotopes of hydrogen in water samples by electrolysis, reduction of the concentrate to gaseous hydrogen over hot zinc and counting of the tritium in a low-background gas counter. Higher geometrical counting efficiency than reported previously has been achieved by use of a counter with flat Saran end plates. The adhesive used in previous counters (Armstrong A-1)* was found to have a relatively high natural radioactive content (>40 dis/min per g) and replacement with Armstrong A-2 (<1 dis/min per g) reduced the background of a 70 ml counter from 3.5 to 1.50 c/min with anticoincidence shielding inside 3 in. of lead. The counter used in this work has been calibrated with dilutions of several standard solutions prepared by the Radioactivity Standardization Section, Atomic Energy of Canada Ltd., for intercomparison with the National Bureau of Standards, Washington and AERE, Harwell.

During isotopic concentration, the electrolytic gases were discharged from the cells through silica gel drying tubes to prevent condensation of atmospheric moisture in the cooled cells. This has been most important when analysing low-level samples in recent years when the atmospheric tritium concentration has been high. Most analyses were done on 100 ml water electrolysed to 60 mg, of which 5 mg was used for deuterium analysis, 55 mg for Geiger counting as hydrogen with argon and ethylene using an electronic quench circuit. In some cases, 10 ml samples were used for analysis and would have been sufficient for many others.

TRITIUM IN OTTAWA RAIN AND RIVER WATER

The tritium concentration in rainwater has been determined at 1-2 week intervals from 1953 to the present time. BROWN and GRUMMITT (1956) presented individual analyses for 1953-1954. Data for the whole period 1953-1959 are

* Armstrong Products Co., Warsaw, Indiana.

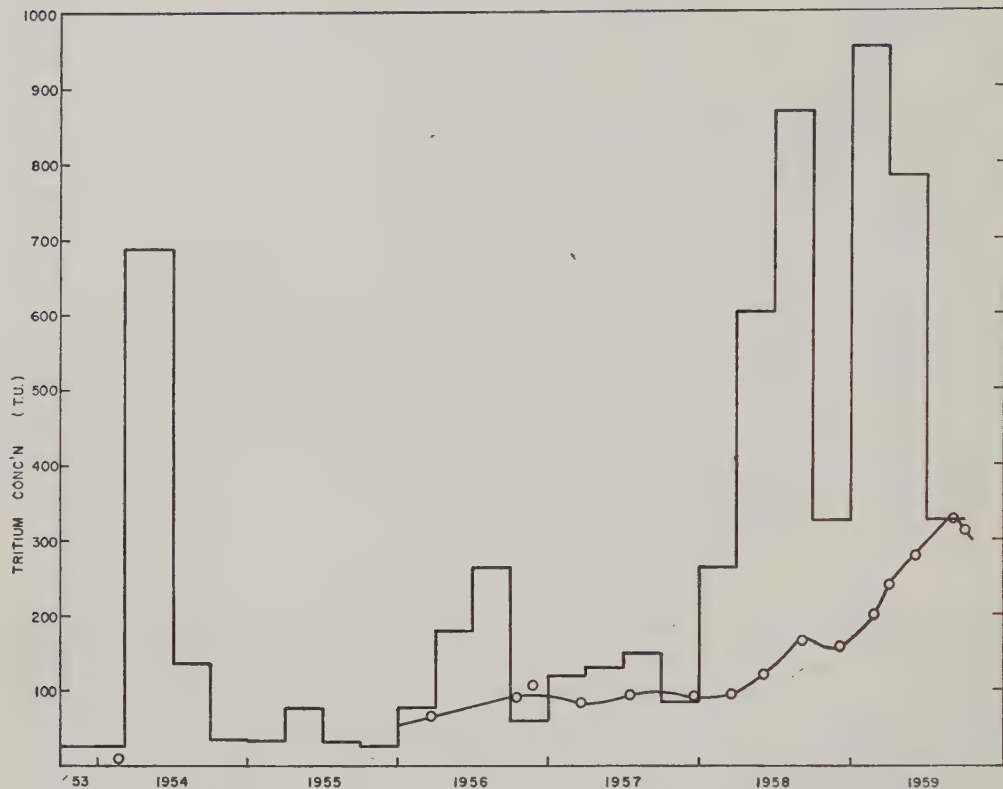


Fig. 2. Tritium in the Ottawa Valley 1953-1959. Step function—measured tritium concentrations of Ottawarain (quarter-year averages). ○—Measured tritium concentrations of Ottawa River water.

summarized in Table 1, Fig. 2, as quarterly averages derived from a smoothed curve drawn through data of frequent spot analyses. The data were relatively insensitive to method of averaging or even rainfall weighting for quarterly periods.

In the writer's previous paper (BROWN and GRUMMITT, 1956), it was considered that there was negligible bomb tritium in the rainwater of the latter half of 1953 and early 1954; the average concentration of 26.6 Tritium units* observed during this period was taken to represent the cosmic-ray tritium level at Ottawa. However, observation of the behaviour of tritium from subsequent U.S.S.R. tests indicates that there probably was tritium from the U.S.S.R. test of August 1953 present during this period. For example, tritium from the U.S.S.R. tests of October 1958 continued to appear in Ottawa rain at close to maximum concentration 8 months later. The early data of KAUFMANN and LIBBY (1954) and von BUTTLAR and LIBBY (1955) are in agreement with such behaviour. Thus, the average of their values for the period December 1952–July 1953 is 7.5 T.U. whereas their average for the period September 1953–February 1954 is 13.8 T.U. GILETTI *et al.* (1958) report rain tritium data for late 1953 and early 1954 at Palisades, N.Y., averaging to a value of 8.5 T.U., but weather patterns portrayed in the

* 1 Tritium Unit (T.U.) = 1 tritium atom per 10^{18} hydrogen atoms.

Table 1. Correlation of tritium in Ottawa rain and river water
(Tritium concentration units: T atoms per 10^{18} H atoms)

Period (in quarters)	Observed rain water T concentration	Calculated storage water T concentration (at end of period)		Observed river water T concen- tration	Collection dates of river samples
		$x = 0.30$ No fractionation i.e. $B = C = 1.0$	$x = 0.27$ $B = 1.06$ $C = 0.94$		
1948				20.4	1948
1949				8.9	9 Feb. 1949
1950				* 11	22 Aug. 1950
1951				17.6	16 Jan. 1951
1952				16.6	13 July 1952
1953-2	15.3†	12.9	14.0		
3	25.8	13.7	14.6		
4	27.8	14.5	15.4		
1954-1‡	27.6	15.1	15.9	10.3	12 March
2§	688	78.1	77.5		
3	137	81.4	81.4		
4	35	77.0	77.4		
1955-1	33	73.0	73.6		
2	78	72.4	73.5		
3	33	68.7	70.1		
4	27	64.8	66.6		
1956-1	79	65.1	67.0	66.7	20 April
2	180	72.5	74.3		
3	265	85.3	87.0		
4	59	82.4	84.5	92.5	Nov.
				108	21 Dec.
1957-1	120	84.0	86.4	86.4	18 April
2	132	86.3	88.9		
3	151	89.8	92.5	96.9	24 Aug.
4	86	88.3	91.4	92.7	17 Jan. 1958
1958-1	264	100	103	95.6	17 April
2	603	135	137	122	30 June
3	868	185	187	167	30 Sept.
4	325	192	195	157	29 Dec.
1959-1	953	245	247	200	20 Mar.
				241	1 May
2	783	280	283	280	3 July
3	327	280	285	327	30 Sept.
				306	30 Oct.
4	102	263	271	275	2 Feb. 1960

Symbols B , C , x defined in text.

* Ottawa Laboratory Reagent Solutions.

† Estimated from 1953-3,-4 Ottawa data and LIBBY *et al.* Chicago data (see text).

‡ January and February 1954 only.

§ March-June 1954 inclusive.

Climatic Atlas of the United States (VISHER 1954) suggest that an appreciable portion of the precipitation could be brought in by weather sweeping up the east coast of the United States and hence be derived more directly from the ocean, and lower in tritium for this reason.

It is probable that tritium from tests at the U.S. Pacific Proving Ground in 1951 and 1952 behaved in a manner similar to that of U.S. Tests in 1954, 1956 and 1958, i.e. the appearance of peak tritium concentration soon after the tests and subsequent exponential washout. The minor nature of any peak in Chicago rain during November and December 1952 indicates the relatively insignificant contribution that subsequent washout of bomb tritium during the period December 1952–July 1953 would make to the natural level. Hence, data for this period should be a good measure of cosmic tritium.

Adjusting the Ottawa average for that part of 1953 after the U.S.S.R. test (28.2 T.U.) by the ratio 7.5/13.8 (data of LIBBY *et al.*), a value of 15.3 T.U. is obtained for the tritium level of Ottawa rain in the first half of 1953. This is now considered to be the concentration of cosmic-ray produced tritium in Ottawa rain. An intercomparison of samples with BEGEMANN (1956) has indicated that this laboratory obtains results 30 per cent higher than the Chicago group, half of the discrepancy originating in the electrolysis step, half in the counting. Even when this discrepancy is allowed for, an appreciable difference remains between the tritium concentration reported for Chicago rain and that reported here for Ottawa rain.

Some data, included in Table 1, have been obtained on the tritium concentration of Ottawa River water in the pre-bomb period by analysing dated reagent solutions which had been unused and reasonably well sealed during the last few years in an Ottawa laboratory not associated with radioactive materials. Such samples are always suspect as to the possibility of contamination during storage by the high atmospheric tritium levels experienced in recent years, but they serve to set an upper limit in any case. The average value will be seen to be consistent with a pre-bomb rainwater tritium concentration of about 15 T.U.

Table 1 also presents the results of periodic analysis of Ottawa River water sampled at Deep River. These data are plotted in Fig. 2 at 30 days prior to the actual sampling date to allow for the average transit time of water in the river from the center of the drainage area to the river sampling point (150 miles at 5 miles per day).

THE HYDROLOGICAL MODEL

To correlate the tritium content of rain and river water, let us consider a simplified model of the system consisting of condensed atmospheric moisture (clouds or falling rain) of tritium concentration T_R , fresh precipitation on the ground or in vegetation in rapid interchange with atmospheric water and, hence, also of tritium concentration T_R , and a storage reservoir, the major constituent of which is the ground water, but including other storage units such as lakes, streams and soil. ERIKSSON (1958) has pointed out that although it is highly unlikely that the stored water of a district is rapidly mixed, a range of transit times of multiple isolated drainage channels will probably produce conditions of concentration in a stream approximating those of drainage from a rapidly mixing reservoir. On this

basis, the water complement of the basin may be considered as being in a rapidly mixed reservoir sampled by the river, the tritium content of which is, thus, a measure of the average for the whole storage reservoir.

Tritium is introduced into the surface-groundwater system by the deposition of rain of tritium concentration T_R and leaves the system by: (1) radioactive decay; (2) discharge of river water of tritium concentration T_V ; (3) evaporation of water at tritium concentration T_E . A fraction, f , of the evaporated water may be considered to be fresh rainwater, the remainder mixed storage water. The tritium concentrations of these components will be reduced by isotopic fractionation and in this instance can only be estimated by successive approximations. The evaporated tritium is reincorporated in the tropospheric moisture of the district and participates in establishing the tritium concentration of the rainwater. To maintain a simple model, any net gain or loss of evaporated tritium with adjacent districts will be considered negligible. This is reasonable if surrounding districts are of similar terrain, but unacceptable for adjacent regions of grossly different hydrologic character such as desert or large bodies of water.

Thus, the tritium balance of the system as represented by this model consists of:

$$\begin{array}{ccccc}
 \text{annual influx} & & \text{reservoir} & & \text{annual efflux} \\
 R.T_R & \longrightarrow & V.T_V & \longrightarrow & (1) \lambda V T_V \\
 & & & & (2) a R T_V \\
 & & & & (3) E.T_E = (1-a)R[fbT_R + (1-f)cT_V]
 \end{array}$$

where T_R = tritium concentration in rainwater;

R = annual rainfall;

T_V = average tritium concentration in storage water of the valley;

V = stored water reservoir of the valley;

λ = decay constant of tritium (years⁻¹);

a = fractional runoff;

T_E = tritium concentration in evaporated water;

E = annual evaporation = $(1-a)R$;

f = fraction of fresh precipitation in evaporated water;

b = tritium-hydrogen fractionation factor for evaporated rainwater relative to deposited rainwater;

c = tritium-hydrogen fractionation factor for evaporated groundwater relative to non-evaporated storage water.

The storage water reservoir, V , and the evaporative feedback characteristic, f , are the unknown factors in the above relationships about which we might hope to gain information from observance of the correlation of T_R and T_V .

With the magnitude of the water reservoir of the valley, V , remaining constant, fluctuation of the tritium inventory is described by the equation:

$$\begin{aligned}
 V \frac{dt_V}{dt} &= R.T_R - \lambda V T_V - (1-a)RfbT_R - (1-a-f+af)RcT_V \\
 &= Rb(1-f+af)T_R + (1-b)RT_R - [Rc(1-f+af)]T_V - (1-c)aRT_V - \lambda V T_V
 \end{aligned}$$

Putting $x = (1 - f + af)R/V = \frac{\text{non-evaporated rain per annum}}{\text{storage reservoir}}$
 $= \text{fractional replacement of reservoir per annum}$

$$\frac{dT_V}{dt} = \left[b + \frac{(1-b)}{1-f+af} \right] \chi T_R - \left[c + \frac{(1-c)a}{1-f+af} \right] \chi T_V - \lambda T_V \quad (1a)$$

$$= B \chi T_R - (Cx + \lambda) T_V \quad (1b)$$

where $B = b + \frac{(1-b)}{1-f+af}$ and $C = c + \frac{(1-c)a}{1-f+af}$

If T_R can be integrated with time in some manner and the fractionation parameters B and C estimated, integration of equation (1b) will give a relationship between T_V and T_R from which x , the turnover rate constant of water in the system in terms of the fraction of the reservoir replaced per annum, may be deduced. In practice, we will use this relationship to predict T_V figures from measuring T_R data for several values of x . Comparison with the experimentally observed values of the tritium content of river water over a period of fluctuating rainwater tritium concentration will test the model and yield a value of x for the system under study if the model is adequate.

The irregular nature of the tritium level in rainwater as a result of injections of bomb tritium precludes describing T_R by a continuous integrable equation over any appreciable portions of the last few years. In the pre-bomb period, T_R had been relatively constant, on the average, for a long time, equilibrium had been established and $dT_V/dt = 0$

$$T_{V,\text{equil}} = \frac{Bx}{Cx + \lambda} T_R \text{ cosmic} \quad (2)$$

During some periods following injection of large amounts of bomb tritium, T_R has shown an approximately exponential fall, but in general, T_R has fluctuated irregularly and is treated here as a series of independent quarterly averages. Integration of equation (1b) on this basis leads to the following general equation describing the correlation of the concentration of tritium in the storage reservoir with its concentration in rainwater:

$$T_{V_n} = \frac{Bx}{Cx + \lambda} T_{R_n} [1 - \exp[-(Cx + \lambda)t]] + T_{V_{n-1}} \exp[-(Cx + \lambda)t] \quad (3)$$

where T_{R_n} = average T_R for the n th period;
 T_{V_n} = T_V at the end of the n th period;
 $T_{V_{n-1}}$ = T_V at the end of the preceding period;
 t = length of the period.

TURNOVER RATE OF THE UPPER OTTAWA STORAGE RESERVOIR

In a first approximation, these equations will be simplified by disregarding isotopic fractionation on evaporation, i.e. say $b = c = 1.0$, hence $B = C = 1.0$. In Fig. 3, T_V calculated from measured T_R data using this simplified version of

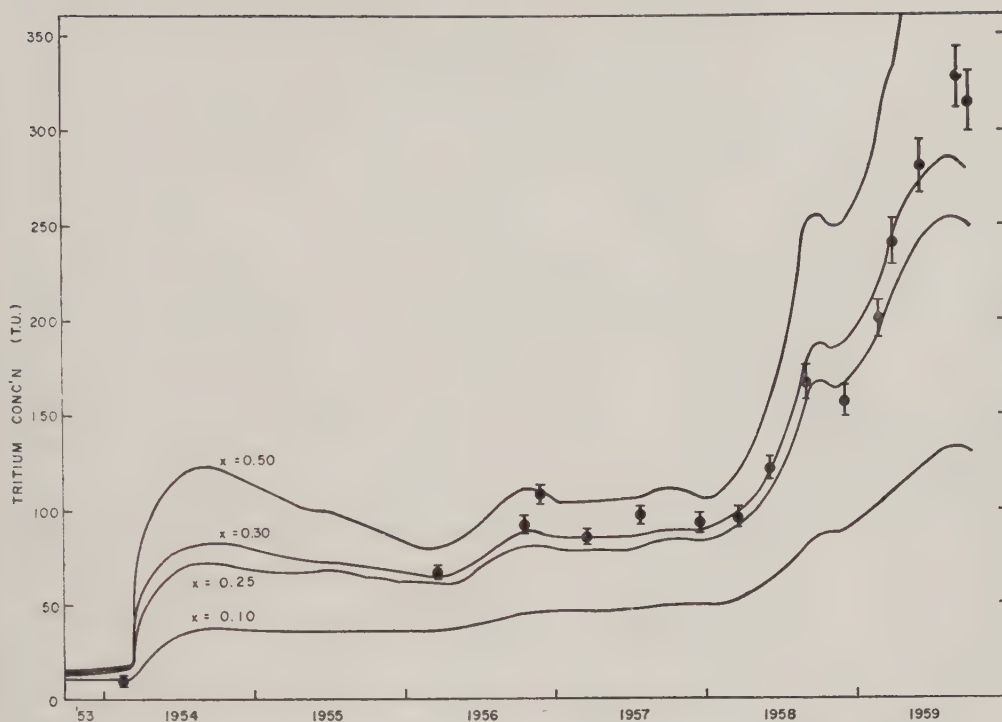


Fig. 3. Comparison of measured Ottawa River water tritium concentrations, $\bullet$, with calculated storage water tritium concentrations (equation (3)) for various turnover rates, neglecting evaporative fractionation effects. Curves calculated on monthly basis for periods of sharp inflection, otherwise on a quarterly basis. Calculated storage water tritium curve for $x = 0.27$ and fractionation conditions $B = 1.06$, $C = 0.94$, is essentially identical to the curve for $x = 0.30$, no fractionation.

equations (2) and (3), is plotted against time for several values of x and compared to tritium concentrations observed in Ottawa River water. A turnover rate constant of 0.30 year^{-1} correlates the calculated and measured values reasonably well over the whole period studied. In periods of rapid change in late 1958 and 1959, the river water tritium concentration overshoots changes predicted by the model both on downward (late 1958) and upward (mid-1959) trends. Evidently there is a greater proportion of rapid drainage than is provided in the model by the assumption of equivalence to a rapidly mixed water reservoir.

The lack of any obvious seasonal discrepancy indicates the surprisingly minor effect that winter hold-up of fresh precipitation on the ground as snow has on the flux of water through the system.

Evaporative fractionation effects

Evaluation of the evaporative fractionation parameters B and C requires knowledge of a and f as well as the $\text{HTO}-\text{H}_2\text{O}$ separation factor. The fractional runoff, a , may be estimated from the drainage rate and area of the river basin and is known to be about 0.45 for the Ottawa Valley above Deep River from surveys made in connection with hydroelectric power sites (FARIS, 1958). While f could be

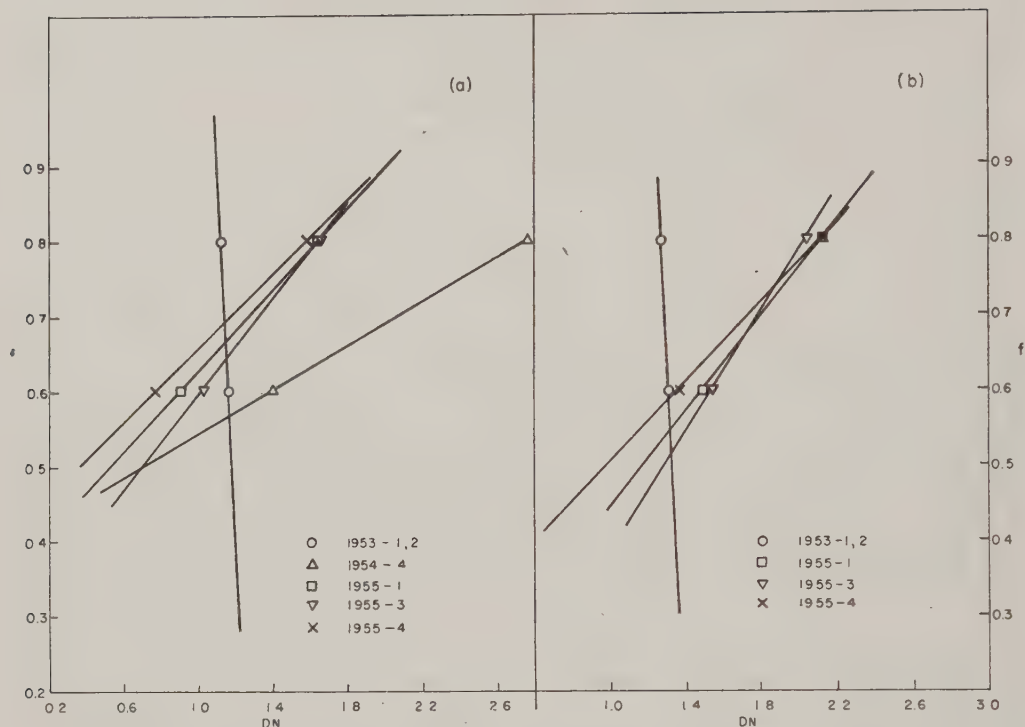


Fig. 4. Dependence of net deposition rate D_N on fraction of fresh precipitation in evaporation rate, f . (a) No allowance for evaporative fractionation: turnover rate constant $x = 0.30$ year⁻¹. (b) Allowance made for evaporative fractionation: turnover rate constant $x = 0.27$ year⁻¹; fractionation factors $b = 0.87$, $c = 0.84$.

measured for particular locations by tritium measurements on evaporating surface and ground waters, it would be difficult to arrive at an overall representative figure. On the other hand, an estimate of f may be deduced from observation of the influence of re-evaporated bomb tritium on the concentration of rainwater tritium during periods in which no new bomb tritium is being introduced.

The concentration and deposition rate of "new" (i.e. non-evaporated) tritium in rainwater may be calculated:

$$T_N = T_R - T_E E/R = T_R - (1 - a)cT_V - (1 - a)(bT_R - cT_V)f \quad (4)$$

$$\text{and} \quad D_N (\text{atoms/cm}^2 \text{ sec}) = 0.85 T_N (\text{T.U.}) \times \text{rainfall (m/quarter year)} \quad (5)$$

where the factor 0.85 arises from the units used.

Not having experimental data for T_r during the period of interest, values from the curve of Fig. 3, Table 1, corresponding to $x = 0.30$ will be used. As previously, isotopic fractionation on evaporation will be disregarded in the first instance.

Because of the small difference in tritium concentration of rain and river water in the pre-bomb era, D_N in this period was relatively insensitive to f , as shown in Fig. 4(a), and the range $f = 0.3$ to 0.8 only affects D_N by 10 per cent. On the other hand, during the portions of 1955 when it may be considered that all new tritium was of cosmic origin, a D_N equal to the pre-bomb value could only be

Table 2. Dependence of net deposition rate on fraction of fresh precipitation in evaporate

$$T_N \text{ (tritium units)} = T_R[1 - (1 - a)bf] - (1 - a)c(1 - f) T_V$$

$$D_N \text{ (atoms/cm}^2 \text{ sec)} = T_N \times 0.85 \times \text{rainfall (m per quarter)}$$

Date	Ave. T_R	Ave. T_V	Rainfall (m/quarter)	T_N		D_N	
				$f = 0.6$	$f = 0.8$	$f = 0.6$	$f = 0.8$
A. No Allowance for Fractionation: $x = 0.30, b = c = 1.0, a = 0.45$							
1953-1, 2	15.3	12.9	0.185	7.4	7.1	1.16	1.12
1954-4	35	79	0.310	6.0	10.9	1.39	2.76
1955-1	33	75	0.189	5.6	10.2	0.90	1.64
-3	33	71	0.179	6.7	10.8	1.02	1.64
-4	27	67	0.244	3.7	7.7	0.77	1.59

(From Fig. 4(a), a common D_N requires $f = 0.67 \pm 0.1$ on basis of ± 5 per cent error on T_R and T_V averages.)

B. Allowance for Fractionation: $x = 0.27, b = 0.87, c = 0.84, a = 0.45$

1953-1, 2	15.3	14.0	0.185	8.3	8.1	1.31	1.28
1954-4	35	79	0.310	10.2	14.1	2.69	3.72
1955-1	33	76	0.189	9.3	13.2	1.49	2.12
3	33	72	0.179	10.1	13.5	1.54	2.05
4	27	68	0.244	6.6	10.2	1.32	2.12

(From Fig. 4(b), a common D_N requires $f = 0.55 \pm 0.1$ on basis of ± 5 per cent error on T_R and T_V averages.)

achieved within the range $f = 0.67 \pm 0.10$, in spite of the wide limits of error on the data. The high D_N for 1954-4, which is discarded in this consideration, perhaps indicates the presence of tailings of Castle tritium. However, the samples analysed for this period were not associated with the storms which accounted for the abnormally high precipitation of the quarter, hence they probably are not representative of the quarter's rain. On the other hand, the low T_R of 1955-4 was associated with easterly storms in October and is compensated for by the above average amount of rainfall resulting from these storms. Easterly storms probably bring in more oceanic moisture than is the case for the prevailing north-westerly to south-westerly weather.

Using this estimate of f to calculate the fractions of rain and storage water unevaporated as 0.63 and 0.92, respectively, the extent of evaporative fractionation may be estimated. The enrichment of the liquid phase is given by:

$$(\text{fraction of liquid remaining})^{1/\alpha-1} - 1$$

where α is the evaporative separation factor for HTO-H₂O. CRAIG *et al.* (1956) suggest that evaporative processes in nature approximate molecular distillation more closely than equilibrium distillation, hence α will involve the square root of

the molecular weights of the species H_2O , HTO as well as their vapour pressures. Information on the vapour pressure of HTO is surprisingly meagre in the literature. Values reported by PRICE (1958) seem unduly low in view of HDO data. BERTSCHE (1958), quoting unpublished data of Los Alamos and the Savannah River Project, reports the vapour pressure of HTO to be 118.8 mm at 56.4°C . In accord with this, assuming the temperature dependence of HTO vapour pressure is similar to that of HDO , are measurements by ROY (1959) and, independently, the writer which give a value of 0.90 for the ratio of vapour pressures of HTO and H_2O at 10°C . In ROY's measurements, simultaneously determined $\text{HDO}/\text{H}_2\text{O}$ vapour pressure ratios agreed with literature data. On the basis of this value at 10°C :

$$\alpha_{\text{H}_2\text{O}}^{\text{HTO}} = \frac{1}{0.90} \sqrt{\left(\frac{20}{18}\right)} = 1.17$$

An enrichment of 0.073 is found for the non-evaporated rainwater corresponding to a depletion of 0.12 of the evaporated portion and $b = 0.88$. Non-evaporated storage water is enriched to the extent of 0.013, evaporated storage water depleted by 0.15 and $c = 0.85/1.013 = 0.84$.

When these initial estimates of f , b and c are inserted in equations (2) and (3), they are found to give calculated T_V 's that correlate with the measured values more closely for $x = 0.27$. Application of the fractionation factors to equations (4) and (5) and the newly calculated T_V data of Table 2B allows a second approximation to be made in which $f = 0.55 \pm 0.10$ is derived from Fig. 4(b). The factors b and c prove to be insensitive to f in the range $f = 0.25$ to 0.75 and no further consideration is warranted. Final values of $B = 1.06$ and $C = 0.94_3$ for equations (1), (2) and (3) are obtained and Table 1 includes T_V values based on these figures and $x = 0.27$. Good correlation of calculated T_V with the experimental data is maintained except for the overshoots in late 1958 and mid-1959 noted previously. The model describes the actual system adequately enough to accept the turnover rate indicated as a long term average. The net deposition rate of cosmic tritium is found to be 1.32 ± 0.10 atoms/cm² sec.

One result of these fractionation effects is that the equilibrium storage water tritium concentration is greater than the rainwater tritium concentration in a system with a turnover rate greater than 0.5 per annum.

DEPOSITION RATE OF COSMIC AND BOMB TRITIUM

In the preceding section and Table 2B, the net deposition rate of cosmic tritium at Ottawa has been deduced to be 1.32 ± 0.1 T atoms/cm² sec. The cosmic production rate will be somewhat greater than this figure to provide for radioactive decay in that portion produced and held for some time in the stratosphere. BEGEMANN and LIBBY (1957) obtained a figure of 1.2 (uncorrected for stratospheric storage) from considerations of the continental water balance and their tritium measurements of Mississippi River water, New York and California rain. However, BOLIN (1958) deduced a figure of 0.7 from the data of LIBBY and co-workers using a hydrodynamic model somewhat similar to the one developed in the foregoing sections. When the Chicago data for early 1953 rain and river water (7.3 and 6.0 T.U., respectively) are treated according to the model of this paper (equations

Table 3. Net tritium deposit at Ottawa

$$T_N = T_R(1 - bf + af) - T_Vc(1 - f + af - a)$$

$$= 0.74T_R - 0.21T_V$$

$$\text{T deposit (atoms/cm}^2\text{)} = T_N(\text{T.U.}) \times R(\text{m/year}) \times 6.7 \times 10^6$$

Date	Ave. T_R	Ave. T_V	Ave. T_N	Annual rainfall (m)	T deposit (atoms/cm ² per year)
pre 1953	15.3	14.0*	8.4	0.74†	4.2×10^7
1953	21.1	14.4*	12.6	0.746	6.3×10^7
1954	277	51*	194	1.11	145×10^7
1955	43	72*	17	0.719	8.2×10^7
1956	145	78	89	0.800	48×10^7
1957	122	92	70	0.734	34×10^7
1958	537	132	362	0.855	208×10^7
1959	541	270	343	0.893	205×10^7

* From calculated T_V values of Table 1 for $x = 0.27$, $B = 1.06$, $C = 0.943$.

† Rainfall rate of period during which cosmic tritium concentration was estimated, i.e. latter half of 1953.

(4) and (5)), assuming f , b and c factors found for the Ottawa valley are applicable to the upper Mississippi valley, a value of $0.71 \text{ atoms/cm}^2 \text{ sec}$ is obtained. Thus, there remains a considerable disparity between Ottawa and Chicago deposition rates beyond that accounted for by demonstrated analytical discrepancies of 30 per cent.

Table 3 presents a summary of the net deposition of tritium at Ottawa up to the end of 1959. While this data is only applicable to the Ottawa rain area in the strictest case, it should be valuable as an indication of the amount of deposition generally in the northern hemisphere. Bomb tritium deposited over the 7-year period amounted to eight times the natural tritium inventory indicated by the pre-1953 deposition data. Allowing for radioactive decay, the inventory of deposited bomb tritium at the end of 1959 was 7.3 times the natural tritium inventory, much of which is in the deep ocean waters. Deposition of bomb tritium following the tests of 1958 (Fig. 2) was much more prolonged than that following the tests of 1954, presumably as a result of stratospheric hold-up. However, by the last quarter of 1959, the net deposition rate was down to twice that of pre-1953.

STORAGE RESERVOIRS

The Ottawa valley

The fractional turnover rate of 0.27 per annum found for the water reservoir of the Ottawa valley indicates a mean residence time of water in the system of 3.7 years. Knowing a and f , it is possible to estimate the magnitude of the water storage reservoir, V , from the relationship $x = (1 - f + af)R/V$. Thus, for the Ottawa valley, the water reservoir (as defined by tritium concentration equal to that of the river) is 2.6 times the annual rainfall, or about 2.1 m. The amount of storage water evaporated per annum is $0.26R$, or $0.1V$, while the amount of re-evaporated rainwater which does not enter the storage system at all is found to

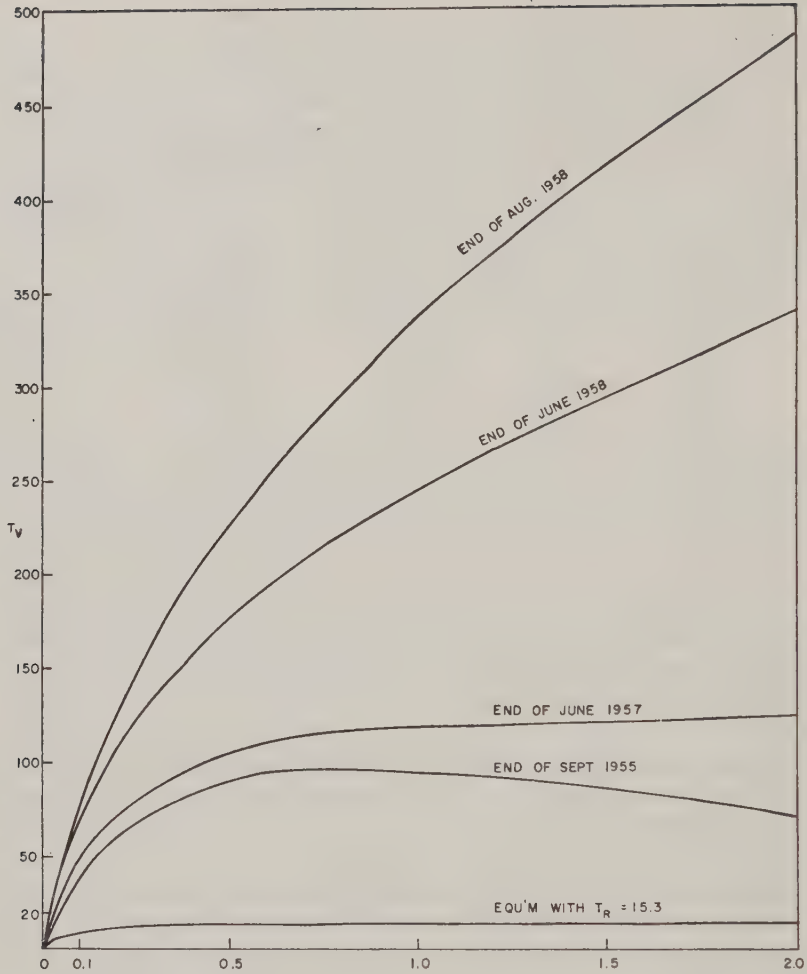


Fig. 5. Calculated storage water tritium concentration (equation (3)) as a function of the turnover rate constant of the system, x , at various times.

be $0.3R$, or 0.24 m per annum. Since maintenance of this latter water at the tritium level of current rainfall in accordance with definitions of the model used requires turnover of this reservoir numerous times a year, the absolute amount of recycling rainwater is small—the atmospheric and surface reservoirs for this water amount to only a few centimetres.

Tributary valleys

The tritium data available may be applied to tributaries of the Ottawa River to determine the turnover rate in terms of the local stream. For this purpose, it is convenient to convert the curves of Fig. 3 to plots of x vs. calculated T_v for specific dates, as in Fig. 5. These prove useful in deducing x from individual samples. The relatively minor effects of fractionation may be neglected. Values

of x for a number of rivers are presented in Table 4. Included are values for Lake Erie and the St. Lawrence River which would be influenced by tritium deposition over areas for which the Ottawa T_R data might not be strictly representative.

Bearing in mind that the turnover rate measured here encompasses both surface and ground water components, the values observed are in the relative

Table 4. Turnover rate of various streams associated with the Ottawa valley

Stream	Date sampled	T concentration observed (T.U.)	x = fractional turnover/year
South Nation R.	28 June 1958	270	1.25
South Nation R.	28 August	478	1.94
Rideau R.	28 June	227	0.84
Rideau R.	28 August	302	0.82
Mississippi R.*	8 July	167	0.45
Madawaska R.	8 July	163	0.43
Gatineau R.	3 August	249	0.8
Petawawa R.	1 July	180	0.51
Ottawa R. (Dozois Reservoir)	3 September	145	0.24
Ottawa R. (Temiskaming)	25 August	215	0.45
Ottawa R. (Deep River)	30 June	122	0.30
Ottawa R. (Deep River)	30 September	167	0.30
Lake Erie (at exit)	14 August	96.1	0.14
St. Lawrence R. (at Brockville)	13 September	67.8	0.085

* A small tributary entering the Ottawa River about 30 miles upstream from Ottawa.

order that would be expected from the terrain involved. The South Nation and Rideau systems of the lower Ottawa valley are largely free of forest and rapid surface runoff and evapotranspiration overshadow the slow ground water turnover indicated by extensive deposits of till, late marine and fluvial muds. In the upper parts of the valley, the ground water reservoir is probably not as extensive, but surface runoff is much less as the result of heavy forest and the overall turnover rate is low. The Mississippi and Madawaska systems originate in such terrain but pass into the lowland plain as they approach the main stream just west of Ottawa. The Gatineau has common headwaters with the Ottawa River but, flowing directly south, passes through rugged terrain with much exposed bedrock where there is rapid surface runoff and little ground water reservoir. The one analysis available suggests that this lower section more than compensates for the headwater conditions.

It would be of great value to conduct extensive tritium measurements on a restricted area such as one of these smaller drainage basins where the hydrologic characteristics could be studied in detail by conventional means at the same time. However, in general application of the method demonstrated here, it should be sufficient to measure the average tritium concentration of rainwater of a district over a period of a few months, perhaps using a single composite sample, and

observe the change effected by this tritium deposit on the local river water tritium level, deducing x from equation (3).

Well waters

Conditions of a pseudo-rapidly mixing reservoir do not exist in the case of direct sources of ground water such as wells and springs and application of the model considered in the foregoing sections is inappropriate. In these cases, feed is through a few confined underground channels from a limited surface source some distance away. Transit time in such channels may be deduced from the lag in appearance of bomb tritium injections or, if longer than the period during which bomb tritium has been released, from the extent of radioactive decay of natural tritium. VON BUTTLAR (1959) has demonstrated the application of this technique to the study of a number of wells in New Mexico.

Table 5. Tritium content of Cole's well, Deep River

Sample	Date	Tritium concentration (T.U.)
T8	11 Feb. 1954	1.78 $\pm$ 0.13
T23	29 July 1958	1.40 $\pm$ 0.12
T39	21 Jan. 1959	0.72 $\pm$ 0.11
T39R	21 Jan. 1959	0.40 $\pm$ 0.09
T42	10 March 1959	1.21 $\pm$ 0.11
T43	26 March 1959	0.69 $\pm$ 0.14
T43R	26 March 1959	1.09 $\pm$ 0.08
T47	1 May 1959	1.27 $\pm$ 0.08
T49	3 July 1959	1.30 $\pm$ 0.08

Sample T8 stored $4\frac{1}{2}$ years before analysis, hence possibility of contamination. Error quoted is statistical counting error only.

A subtraction of 0.15 T.U. has been made in each case to allow for tritium introduced with KOH.

Table 5 presents data for a well in the vicinity of Deep River. The well is drilled to a depth of 150 ft; the water level is at a depth of 120 ft, approximately on a level with the Ottawa River surface some 3000 ft distant. The lack of any effect of thermonuclear tests on the tritium concentration of this well water during the past 5 years shows that there has been insignificant direct feed-in of recent water. The average concentration of 1.1 T.U. indicates that 47 years has elapsed since the well water entered the feed system as rainwater with the natural tritium concentration of 15.3 T.U. Of course, this transit time may be an average of several associated with different feed channels. The variation in tritium concentration observed may be real and explained by fluctuating contributions of several feed channels.

It might be noted that a possible source of tritium contamination in analysing samples of this low level is the hydrogen introduced with the potassium hydroxide electrolyte. The hydrogen of potassium hydroxide used in this work in 1956 analysed 30.6 T.U., that of 1959, 42.3 T.U. Two-thirds of the hydrogen of reagent potassium hydroxide is in the form of water which may be removed by fusion of

the potassium hydroxide. A subtraction of 0.15 T.U. has been made from the analyses of Table 5 to allow for the contribution of the potassium hydroxide, which was not fused in this case. Some workers have avoided such contamination by the use of sodium peroxide, taking care to ensure its complete decomposition before inserting electrodes.

SUMMARY

Observation of the tritium concentration of rain and river water in the Ottawa Valley over the past few years has allowed testing of a hydrologic model which gives information on the characteristics of the system. The model provides estimates of the tritium concentration of the storage water of the valley during earlier intervals from which it is possible to derive the net deposition rate of cosmic and bomb tritium. The correlation of the tritium concentration of rain and river water provided by the model is useful in estimating turnover rates of other water systems in the general vicinity.

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Hydrothermal stability studies of the zircon–thorite group*†

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Abstract—The stability relations among minerals of the zircon–thorite group and the effect of related oxides on them have been studied under both “dry” and hydrothermal conditions. The problem of “hydrous” zircons and its relation to the metamict state has been investigated both experimentally and theoretically. From the data it appears that hydrous zircons and thorites do not involve OH[−] substitution for O^{2−} with omission of Si⁴⁺, but rather are formed by strong water adsorption in metamictized zircon and thorite. The phase equilibrium involved in the thorite–huttonite polymorphism has been studied and it is concluded that huttonite is the only stable polymorph of ThSiO₄. Zircon dissociates at 1550 ± 50°C to ZrO₂ + SiO₂.

The Alkemade triangles in the ternary systems ZrO₂–ThO₂–SiO₂ and ZrO₂–UO₂–SiO₂ have been determined and a not-impossible diagram is presented for the system ThO₂–UO₂–SiO₂. The extent of solid solution between ZrSiO₄–ThSiO₄, ZrSiO₄–“USiO₄” and ThSiO₄–“USiO₄” is discussed in connexion with the composition of natural zircon and thorite. The application of the experimental data to natural mineral assemblages is discussed.

INTRODUCTION

IN RECENT years mineralogical and geochemical investigations of minerals of the zircon–thorite group have increased enormously. It is unfortunate, however, that up until the present time, little was known concerning the chemical equilibria existing among the several minerals of this group.

Geologically, zirconium, hafnium, thorium and uranium are localized in the earth’s crust during the later stages of magmatic activity and crystallize primarily as orthosilicates or oxides in the hydrothermal veins and pegmatites associated with granodiorites and alkaline syenites. Of particular importance to the mineralogist are the phase relations among the zircon, thorite, thorianite and uraninite of such deposits in so far as these equilibria point towards the mechanisms of formation and give definite information about the temperature–pressure–composition environment from which these minerals crystallized.

It is well known, however, that “ordinary” granites and other igneous rocks account for by far the greatest proportion of zirconium, thorium, etc., in the earth’s crust. Zircons have long been recognized as ubiquitous minerals in almost every kind of igneous, sedimentary and metamorphic rock. The overall distribution of zircon in rocks and mineral deposits has prompted its use as a geochronometer (LARSEN *et al.*, 1952) which takes advantage of small amounts of thorium, uranium and lead usually found in analyses of zircons. Many questions have arisen, however, as to whether or not the analysed uranium actually resides in the mineral lattice. A further question arises as to the ability of the zircon

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† Tabular material supplementary to this article (lists of individual runs) has been deposited as Document number 6338 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C. A copy may be secured by citing the Document number and by remitting \$2.50 for photoprints, or \$1.75 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

lattice to retain in solid solution the daughter product lead from the disintegrating uranium isotopes, or whether lead is exsolved from the lattice and becomes subject to external leaching actions.

In addition to uranium and thorium a number of other elements enter the zircon and thorite lattices in diadochic substitution, but only a few quantitative studies have been made on the distribution of such elements as sulphur, yttrium, cerium, lead, niobium, phosphorus and rare earth elements in these minerals (MUENCH, 1934; KOSTYLEVA, 1939; LARSON *et al.*, 1953; HAYASE, 1954; DENNEN and SHIELDS, 1956; NORTON, 1957). The limits of solid solution of these elements in zircon or thorite are unknown and have never been determined experimentally.

The unusual occurrence of zircons and thorites in the metamict state has been known since the last century (BROEGGER, 1893). Thorite is rarely found in a fully crystalline state. Of late sufficient interest has been shown in metamict zircons and thorites and the conditions which bring about this phenomenon (BOROVSKY and BLOKHIN, 1937; HURLEY and FAIRBAIRN, 1952; KULP, *et al.*, 1952; PABST, 1952; FRONDEL, 1953; POVARENENYKH, 1956) to warrant further detailed investigation of the temperature–pressure–compositional environments which may or may not be conducive to the formation of these so-called amorphous, hydrated counterparts of zircon and thorite.

The recent claims of FRONDEL *et al.* (1954) and of HOEKSTRA and FUCHS (1956) on the syntheses of cyrtolite, thorogummite and coffinite (the so-called hydroxylated analogues of zircon, thorite and “ USiO_4 ”, respectively) can bear further examination. If hydroxyl tetrahedra substitute for silicate groups in the zircon lattice a solid solution series must exist between ZrSiO_4 and “ Zr(OH)_4 ”. It is obvious that a phase equilibrium study of the system ZrO_2 – SiO_2 – H_2O should be able to set the stability limits of such a series. The mineralogical interpretation of assemblages of zircon, thorite, uraninite and thorianites have heretofore been handicapped by the lack of equilibrium data on the binary and even unary systems involving ZrO_2 , ThO_2 , UO_2 , SiO_2 and H_2O , especially at low temperatures and under water pressure. If the solid solution limits of, for example, “ USiO_4 ” in zircon are known as a function of temperature and pressure, an assemblage of $\text{UO}_2 + \text{ZrSiO}_4 + \text{SiO}_2$ in which the amount of UO_2 in zircon is known could be shown to have formed in a given temperature–pressure environment from the phase equilibrium data.

It is apparent that the solution to any of the above problems is intimately associated with the solution of one or more of the others. For this reason, it is felt that the problem before us is a basic study of the stability relations and the subsolidus phase equilibria in the systems ZrO_2 – ThO_2 – SiO_2 – H_2O and ZrO_2 – UO_2 – SiO_2 – H_2O and ThO_2 – UO_2 – SiO_2 – H_2O . To solve many of the problems concerning minerals of the zircon–thorite group such studies are fundamental, even though the results therefrom may not directly answer any particular geological problem.

PREVIOUS WORK

Previous work in the binary systems ZrO_2 – ThO_2 , ZrO_2 – UO_2 and ThO_2 – UO_2 has been summarized by the writers (MUMPTON and ROY, 1960) and will not be repeated here. The subsolidus phase equilibria in these systems as well as partial

data for the systems $\text{ZrO}_2\text{--UO}_2\text{--O}$ and $\text{ThO}_2\text{--UO}_2\text{--O}$ have also been reported in this paper.

The system $\text{ZrO}_2\text{--SiO}_2$ contains only one compound, the orthosilicate zircon, the melting point or dissociation temperature of which has long been in question. The conflicting opinions of several authors have been adequately reviewed by CURTIS and SOWMAN (1953) who themselves studied the rate of thermal dissociation and reassociation of this mineral. From their data they concluded that zircon is at no temperature in equilibrium with liquid, but that it dissociates at approximately 1540°C , some 135°C below the temperature of the eutectic between SiO_2 and $\text{ZrO}_{2(\text{ss})}$. GELLER and LANG (1949), however, reported that zircon melts incongruently at about 1775°C , or about 100°C above the eutectic temperature. Although both sets of authors indicated that about 5 moles per cent silica dissolves in zirconia, no unequivocal proof was offered for this.

TOROPOV and GALAHOV (1956) have presented the only major revision to the phase diagram of the system $\text{ZrO}_2\text{--SiO}_2$ by postulating a two-liquid region between 40 and 70 weight per cent silica, and between 2250°C and 2430°C . This is similar to the two-liquid region in the system $\text{TiO}_2\text{--SiO}_2$ (DEVRIES *et al.*, 1954).

FRONDEL *et al.*, (1954) and FRONDEL and COLLETTE (1957)* have synthesized zircon under hydrothermal conditions between 150°C and 700°C , using mixed gels of zirconia and silica as starting materials. They also report a slight shift in the cell dimensions of the product when synthesized at the lower temperature. This they attribute to the presence of $(\text{OH})_4^{-4}$ tetrahedra substituting for SiO_4^{4-} tetrahedra in the zircon lattice in the manner, $\text{Zr}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$ (see also FRONDEL 1953).

Phase diagrams for the low-temperature regions of the systems $\text{ThO}_2\text{--SiO}_2$ and $\text{ThO}_2\text{--SiO}_2\text{--H}_2\text{O}$ have not been determined up to the present time, although the crystallochemical similarity between zirconium and thorium suggests that the thoria–silica diagram should differ only slightly from its zirconia counter-part. Aside from the fact that only a cubic form of ThO_2 is known, compared with the two or three polymorphs of ZrO_2 , the major difference between the two systems is the fact that thorium silicate occurs in two polymorphic forms, tetragonal thorite and monoclinic huttonite, while only a tetragonal modification of ZrSiO_4 has been observed.

Although a number of heating experiments have been carried out on both huttonite and thorite, the “melting” of ThSiO_4 and the liquidus equilibria are unknown.

In his study of the metamict state, PABST (1952) heated samples of metamict thorite, crystalline uranothorite and a mixture of amorphous silica and ThO_2 progressively up to about 1400°C . The uranothorite sample showed no change even at the highest temperature, although the duration of the runs were not reported. At 1400°C the metamict thorite sample converted to huttonite. Partially metamict thorite samples, when heated, first yielded a mixture of thorite + silica + ThO_2 , and subsequently, above 950°C gave huttonite as the principal phase present. PABST quoted J. BERMAN (by personal communication) as having

* This paper was not published until after the present experimental work had been completed.

found that huttonite samples "... when heated in a water free atmosphere ... 'revert' to the tetragonal variety at a temperature around 1200°C. Likewise, crystalline thorite will form the monoclinic ThSiO_4 when heated high enough in air but does not appear to change when heated in water free helium at our maximum temperature (1300°C)."

FRONDEL and COLLETTE (1957) and FRONDEL *et al.* (1954) reported that thorite and huttonite had been synthesized under hydrothermal conditions between 150 and 800°C, using mixed gels as reactants. Huttonite was favoured in weakly alkaline solutions and could not be converted to thorite hydrothermally or dry. Sintering synthetic thorite failed also to yield huttonite at 1400°C. These authors also claim the presence of hydroxyl water in the thorite lattice at low temperatures.

With the exception of the studies of the above authors, no work has been published on the systems $\text{ZrO}_2\text{--ThO}_2\text{--SiO}_2$, $\text{ZrO}_2\text{--UO}_2\text{--SiO}_2$ or $\text{ThO}_2\text{--UO}_2\text{--SiO}_2$ or their counterparts with water. Five runs in which the starting Zr:U ratio was 1:1 were made by the above authors in the system $\text{ZrO}_2\text{--UO}_2\text{--SiO}_2\text{--H}_2\text{O}$ under hydrothermal conditions. Zircon with expanded cell dimensions plus a cubic phase were produced. Two runs on the $\text{ThO}_2\text{--ZrO}_2\text{--SiO}_2\text{--H}_2\text{O}$ system at the same compositions yielded "slightly expanded" zircon plus normal thorite. On the whole, runs in the system $\text{ThO}_2\text{--UO}_2\text{--SiO}_2\text{--H}_2\text{O}$ yielded thorite plus a cubic phase, starting with a 1:1 $\text{ThO}_2\text{:UO}_2$ ratio.

EXPERIMENTAL

Starting materials

The choice of starting materials for investigations involving tetravalent oxides is a crucial one if equilibrium is to be attained in a reasonable length of time. Both natural (Table 1) and synthetic (Table 2) starting materials were used. Several standard methods of preparing starting mixtures for hydrothermal studies were tried (ROY, 1956) with the best results being obtained by the following method.

Calculated amounts of reagent grade ZrCl_4 , UCl_4 , $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ and SiCl_4 were dissolved separately in absolute ethanol and then thoroughly mixed, with the subsequent addition of distilled water. The combined solution was then added slowly with rapid mixing to an excess of concentrated NH_4OH in a beaker, resulting in the simultaneous precipitation of the hydroxides as gels. The precipitate was digested overnight, filtered and evaporated to dryness and ignited at approximately 350°C for 24 hr in order to drive off any ammonium chloride entrapped in the gel structure. Gel precipitates containing large amounts of UO_2 could not be filtered and therefore were evaporated to dryness and then ignited. All starting gels were amorphous to X-rays and were sufficiently reactive under the experimental conditions, except below 250°C where reactions were apparently incomplete after 1 month. All of the zirconium chemicals used contained the usual Hf/Zr ratio of about 1:50 on an atomic basis. Crystallized oxide mixtures were prepared by heating the appropriate gel at 1350°C overnight.

The starting materials were not analysed since the synthetic procedure is inherently more reliable than analysis. Confidence in their compositions was

Table 1. Results of hydrothermal treatment at 500°C and 60,000 lb/in² pressure of natural metamict minerals

Sample number	Mineral name*	Locality	Products
56-S-54†	Cyrtolite	Rare Earth Mine, Monmouth Tp., Ontario	Well crystallized zircon
56-S-119†	Cyrtolite	Silver Crater Mine, Halburton Co., Ontario	Well crystallized zircon
56-S-36†	Cyrtolite	Saranac Mine, Haliburton Co., Ontario	Well crystallized zircon
56-S-38†	Cyrtolite	Fraser Mine, Haliburton Co., Ontario	Well crystallized zircon
96912‡	Malacon	Ambatofotikely, Madagascar	Well crystallized zircon + some ZrO ₂
104734‡	Zircon	Cash, Oklahoma	Well crystallized zircon
12359‡	Zircon	Arendal, Norway	Well crystallized zircon
106689‡	Ribierite	Macarani, Bahai, Brazil	Well crystallized zircon
92953‡	Cyrtolite	Bedford, N.Y.	Well crystallized zircon + some ZrO ₂ (previously present)
C2968‡	Naegite	Naegi, Japan	Well crystallized zircon + some ZrO ₂
49037‡	Malacon	Hittero, Norway	Well crystallized zircon
394.42§	Cyrtolite	Mt. Antero, Colorado	Well crystallized zircon
W-26	Cyrtolite	Buffalo, Colorado	Well crystallized zircon + trace ZrO ₂
T-25**	Thorium silicate	Montana	Well crystallized thorite

* All minerals were selected because of their poor crystallinity as evidenced by their broad, diffuse X-ray diffraction patterns, if any.

† Specimens collected by J. SATTERLY, Ontario Department of Mines.

‡ Specimens donated by the U.S. National Museum.

§ Specimen from Genth Mineral Collection, Pennsylvania State Univ.

** Specimen described by MINTO (1956).

obtained in use, e.g. by the crystallization of single, homogeneous phases of desired stoichiometry from analogous 1:1 ZrO₂-SiO₂ and 1:1 ThO₂-SiO₂ gels.

Equipment and techniques

The experimental equipment and techniques have been thoroughly described in previous publications.

Atmospheric pressure work up to 1600°C was carried out by the usual quenching method (SHEPHERD *et al.*, 1909). Several compounds were melted in an oxyhydrogen flame, the temperature of the sample being measured by means of an optical pyrometer. Runs made in controlled partial pressures of oxygen were carried out in equipment kindly furnished by Professor A. MUAN. (For a comprehensive review of the methods, apparatus and calculations involved, see MUAN (1958).) The majority of runs were made under water pressures using procedures and equipment described in detail by ROY and OSBORN (1952), ROY and TUTTLE (1956). The samples were all sealed in gold tubes to prevent compositional changes.

Table 2. Starting compositions

Mixture number	ZrO ₂	Molar ratio*		SiO ₂
		ThO ₂	UO ₂	
ZS 11	1.00			1.00
ZS 1.90	1.00			0.90
ZS 1.75	1.00			0.75
TS 11		1.00		1.00
TS 1.90		1.00		0.90
TS 1.75		1.00		0.75
ZTS 112	1.00	1.00		2.00
ZTS 134	1.00	3.00		4.00
ZTS 314		3.00	1.00	4.00
ZTS 538	5.00	3.00		8.00
ZTS 18	0.26	4.51		5.23
ZTS 19	0.50	4.50		5.00
ZTS 20	4.75	0.25		5.00
ZTS 21	4.50	0.50		5.00
ZTS 111	1.00	1.00		1.00
ZTS 113	1.00	1.00		3.00
ZTS 221	2.00	2.00		1.00
ZTS 172	1.00	7.00		2.00
ZTS 712	7.00	1.00		2.00
ZUS 112	1.00		1.00	2.00
ZUS 314	3.00		1.00	4.00
ZUS 1	4.50		0.50	5.00
ZUS 2	1.00		1.00	1.00
ZUS 3	1.50		6.50	2.00
ZUS 4	3.00		1.00	1.00
TUS 112		1.00	1.00	2.00
TUS 314		3.00	1.00	4.00
TUS 1		4.50	0.50	5.00
TUS 2		2.00	2.00	1.00
TUS 3		1.00	3.00	1.00
TUS 4		3.00	1.00	1.00
US 11			1.00	1.00

* Zirconia, thorium, silica and UO₃ were obtained from ZrCl₄, Th(NO₃)₄·4H₂O, SiCl₄, and UCl₄, respectively.

Identification of products

All products were identified by X-ray diffraction using a high-angle Norelco diffractometer and Ni-filtered CuK radiation. The diffraction patterns of the products were compared with standard patterns obtained as pure end members and from the literature. Lattice spacings were used throughout to estimate compositions of solid solutions. Slow patterns were run at $\frac{1}{3}^\circ 2\theta$ per min, and the instrument calibrated against silicon for these measurements. In order to estimate with any degree of accuracy the amount of solid solution between two phases where solid solution is not complete, it was found necessary to assume a straight-line relation between the d -values for selected spacings of the two end-member compounds, and to use this line to calculate the composition of a particular solid

solution after measuring its lattice spacings. It is due to this probably inexact assumption that an accuracy of only ± 2 moles per cent is reported for the compositions of the solid-solution products. For the series ZrSiO_4 -“ USiO_4 ” and ThSiO_4 -“ USiO_4 ” the change in the (200) spacing was used to estimate the amount of solid solution. A hypothetical value for “ USiO_4 ” was estimated from the size relations among Th^{4+} , Zr^{4+} and U^{4+} (see Fig. 1).

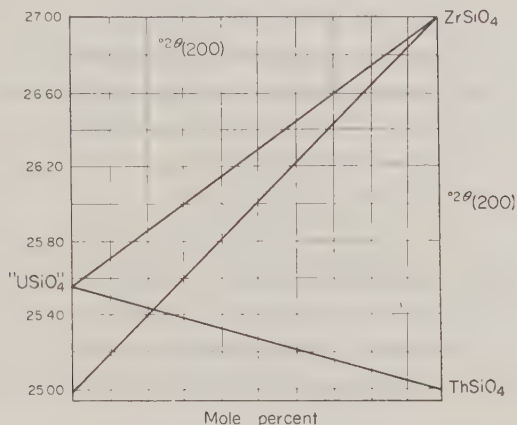


Fig. 1. Plot to determine compositions of uranium-rich solid solutions, assuming a binary relation between composition and cell dimension. The size of the “ USiO_4 ” is calculated by comparing the sizes of the tetravalent ions.

EXPERIMENTAL RESULTS AND DISCUSSION

Over 500 individual runs have been made in the present investigation. Tables 3 and 4 are abstracts of the runs indicating the type of data obtained. A full summary listing all the runs is available in the original thesis by F. A. MUMPTON from the University Microfilms, Ann Arbor, Michigan. The details of all runs and starting materials, in addition to X-ray diffraction spacing shifts of the products, are found in these tabulations of the experimental data.

The system ZrO_2 - SiO_2 - H_2O

In the present study zircon has been prepared dry by heating the 1:1 zirconia:silica gel starting material to about 1300°C for 24 hr. This well crystallized material was then held at higher temperatures for 72 hr and quenched to room temperature. The results indicated that at $1500^\circ\text{C} \pm 5^\circ\text{C}$ zircon apparently did not dissociate, while at $1600^\circ\text{C} \pm 5^\circ\text{C}$ the peaks of monoclinic zirconia appeared in the X-ray diffraction pattern of the product. These data unequivocally establish the conclusions of CURTIS and SOWMAN (1953), that zircon dissociates *below* the eutectic to zirconia and silica. Their data on this temperature are also far from exact but without hydrothermal or otherwise catalysed runs at these elevated temperatures the determination of the exact dissociation temperature would be quite tedious and probably meaningless. The value of $1550^\circ\text{C} \pm 50^\circ\text{C}$ is therefore given for this dissociation temperature.

Although both of the previous sets of authors indicate that about 5 moles per

cent silica dissolves in zirconia, there is no unequivocal proof for this phenomenon. Hydrothermal and "dry" runs at all temperatures from compositions between that of zircon and ZrO_2 have yielded zirconia whose X-ray diffraction spacings are not measurably shifted, and it is therefore felt that the so-called solid solution between zirconia and silica, previously proposed from inconclusive data, may be the result of failure to reach equilibrium or the inability to detect small amounts of silica.

During the present investigation the hydrous zircon problem was investigated in considerable detail. From the fact that forty-three out of seventy-six analyses of zircons in the literature list water as a major constituent there can be little doubt that water is present in the structure of many zircons. The suggestion that it enters the lattice as $(\text{OH})^-$ (FRONDEL, 1953; FRONDEL *et al.*, 1954; FRONDEL and COLLETTE, 1957) and forms a stable phase under a definite set of pressure-temperature conditions is an appealing crystal chemical concept but must be validated experimentally. In another major structural family with independent SiO_4 groups, the garnets, it has been shown that OH^- can proxy for O^{2-} with concomitant omission of some cations. Recent work of ROY and ROY (1957) has shown that the tetrahedral hydroxyl substitution which had been postulated for montmorillonoids and grossularite garnets may be much more limited than first thought.

The formula representing the substitution of silicate groups by hydroxyl tetrahedra in the structure of zircon and thorite is written $\text{Zr}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$. (FRONDEL, 1953). It can be seen that the end result of desilicification or hydroxylation, to the point where $x = 1$, is the compound " $\text{Zr}(\text{OH})_4$ ". Thus, this type of replacement may simply be expressed as solid solution between ZrSiO_4 and " $\text{Zr}(\text{OH})_4$ ". It should be emphasized that this can in no way be interpreted as solid solution between ZrSiO_4 and H_2O . Fig. 2 shows a plot of the molecular compositions of some sixty-nine zircons and thorites the analyses of which were taken from the literature. If water were present in the lattice as tetrahedral $(\text{OH})^{-1}$ groups, replacing silicate tetrahedra, the composition of natural zircons would be expected to fall along the join ZrSiO_4 -" $\text{Zr}(\text{OH})_4$ ". Instead, these analyses lie very close to the ZrSiO_4 - H_2O join, indicating that water of natural zircons is present as molecular water, not $(\text{OH})^{-1}$.

From an experimental point of view it is obvious that the anhydrous compositions of members of the so-called hydroxyzircon series must lie between ZrSiO_4 and ZrO_2 . Under no conditions of complete reaction could a member of this series be expected to form from the zircon composition itself, unless perhaps silica were leached out and removed from the reaction. Using the 1:1 ZrO_2 : SiO_2 composition and others containing less silica, hydrous zircons were not obtained under any temperature-pressure conditions studied in this investigation. The 1:1 composition consistently yielded well-crystallized zircon as low as 250°C under 40,000 lb/in² water pressure in 30-day runs, while those starting materials containing less silica resulted in well crystallized Zircon + ZrO_2 , as would be expected. However, at 200°C and lower, in short runs (less than 1 week) these gels yielded poorly crystallized zircon-like material whose X-ray diffraction patterns consisted of broad diffuse peaks with slightly expanded spacings. This no doubt is

due to the failure of the mixtures to react completely at these low temperatures. The 1:1 $\text{ZrO}_2:\text{SiO}_2$ gel has a statistical distribution of zirconium and silicon “ions” in an oxygen–hydroxyl matrix, not unlike that of zircon. These broad, weak peaks may represent only the partial crystallization of the gel towards zircon. The same phenomena are encountered with almost any composition studied hydrothermally at a sufficiently low temperature.

It is well known that many natural metamict materials may be reconstituted through heat treatments up to 1000°C for several hours. Many metamict zircons have, however, been reported to recrystallize to only monoclinic or cubic zirconia and (in some cases) silica. These phenomena are no doubt due to the differences in

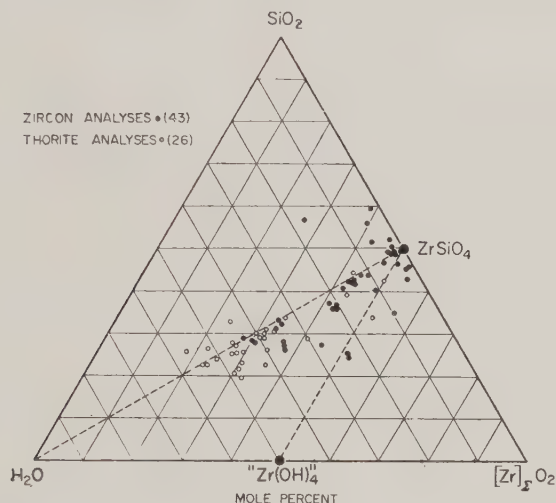


Fig. 2. Composition of natural zircons and thorites plotted on a molecular basis. The symbol $(\text{Zr})_{\Sigma}\text{O}_2$ represents the sum of the elements which might possibly substitute for Zr or Th in these structures. It can clearly be seen that the “hydrous” minerals are not of the type $\text{Zr}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$ which would yield compositions along the join ZrSiO_4 –“ $\text{Zr}(\text{OH})_4$ ”.

the degree of metamictization of the individual zircon. If the lattice is fairly intact and has not been destroyed completely by particle bombardment, it may recrystallize directly to zircon after mild heat treatment. If the lattice is almost completely destroyed, the metamict material is likely to crystallize to $\text{ZrO}_2 + \text{SiO}_2$.

Some fourteen zircons, listed in Table 1, the crystallinities of which were very poor as evidenced by their broad, weak X-ray diffraction patterns, were treated under hydrothermal conditions. All of these minerals were reconstituted to well crystallized zircon at temperatures as low as 500°C under 60,00 lb/in² water pressure after runs of approximately 20 days. It is evident that a close approach to equilibrium has been attained in this hydrothermal environment, whereas dry heating at temperatures below 1200°C , which will not produce zircon even from a gel mixture, may fail to give complete reconstitution of metamict zircon.

Many natural zircons are metamict in part or in whole. The mechanism of the metamictization process has not been firmly established by any of the several authors who have looked into the subject. Both from the analyses plotted in Fig. 2

and from the experimental data of this study it is likely that the zircons found in pegmatites and hydrothermal veins do not contain water as a primary constituent in their structures. Although it is felt that the entry of water is intimately related to the metamict state of zircons, it is more likely that water is a secondary effect of the process, and enters the structure only after the lattice has sufficiently disintegrated. When a zircon grain fulfills the several requirements of metamictization of GOLDSCHMIDT (1924) and BROEGGER (1893) internal radioactive bombardment disrupts the bond forces in the lattice, thereby expanding and partially destroying the structure. In this state, having numerous bonds either broken or strained, the Zr^{4+} and Si^{4+} cations must frequently be displaced to positions where they are surrounded by asymmetrical force fields. This situation combining the open structure of zircon and polarized cation environments is ideal for the entry and strong adsorption of the polar water molecule.

It is more than likely that water molecules are attracted and held to this activated material much more tightly than ordinary adsorbed water, possibly much like the so-called zeolitic water of clays and zeolites. The "slightly-bonded" water idea has been supported by KOSTYLEVA (1946) who found by DTA and weight loss experiments that water was not released from the metamict structure until approximately 200°C.

In several instances slight deficiencies in silica have been noted in metamict zircons. It is not unlikely that in a hydrothermal environment at slightly elevated temperatures, silica may easily be leached from this semiamorphous structure.

It must be concluded that although it has not as yet been realized experimentally, some sort of "solid solution" must exist between metamict zircon and molecular water, *not* " $\text{Zr}(\text{OH})_4$ ". Important data towards the solution of this problem may be obtained from future studies on the artificial metamictization of zircons in connexion with low-temperature hydration experiments.

The system $\text{ThO}_2\text{-SiO}_2\text{-H}_2\text{O}$

In the present study several runs have been made above 1200°C close to the solidus temperature of the system $\text{ThO}_2\text{-SiO}_2$. Thorite and huttonite pellets were heated in an oxyhydrogen flame until melting was observed, and then quenched to room temperature. The resulting product consisted of huttonite + ThO_2 + glassy matrix for both starting materials, which leads to the conclusion that ThSiO_4 like its zirconium analogue, does not melt congruently but either dissociates below the eutectic temperature or melts incongruently to ThO_2 + liquid.* These results prove that the stable polymorph of ThSiO_4 at liquidus temperatures is the monoclinic *huttonite* form,* since not only does it persist, but is formed from thorite. If thorite is regarded as the stable phase in the low-temperature region where it is formed (*vide infra*) the above data lead to the somewhat anomalous situation wherein the high temperature modification is denser (and has lower symmetry) than the lower temperature form. This relation has been observed

* These conclusions have been confirmed by the preliminary data of HARRIS (1959) on the system $\text{ThO}_2\text{-SiO}_2$ published after the present experimental work had been completed. HARRIS reports the incongruent melting of ThSiO_4 at $1975 \pm 50^\circ\text{C}$, to ThO_2 + liquid. He also reported a eutectic at $1700^\circ \pm 10^\circ\text{C}$ between ThSiO_4 and SiO_2 , at 95 mole per cent SiO_2 . No solid solution areas were observed nor was any form of ThSiO_4 other than the monoclinic huttonite polymorph observed.

only in a few other cases of reconstructively related polymorphs, such as boehmite–diaspore, γ - $\alpha^1\text{Ca}_2\text{SiO}_4$ and their isotypes, γ - $\alpha^1\text{Na}_2\text{BeF}_4$, arsenolite–claudetite.

MOONEY (1948, 1950) has shown that the rare earth phosphates, LaPO_4 , CePO_4 , PrPO_4 and NdPO_4 are dimorphous, existing in a high temperature monazite (huttonite type) structure and in a “moderate temperature” hexagonal modification. The lower temperature forms, however, contain about $\frac{1}{2}$ mole of water per unit formula and are described as follows. “In this (hexagonal) structure cerium is co-ordinated to . . . oxygens . . . in such a manner as to form open oxygen-lined channels along the hexagonal axis. The presence of zeolitic water in these channels ($\text{XPO}_4(0.5\text{H}_2\text{O})$) is probably necessary to stabilize the structure.” The monoclinic form of CePO_4 is 25 per cent more dense than the hexagonal modification, similar to the huttonite–thorite relation. The hexagonal forms are probably all metastable throughout.

The present investigation has found that huttonite forms readily from a gel of composition above 1100°C in several hours, although below this temperature, only poorly crystalline ThO_2 can be detected in the products of “dry” quench runs. *Well crystallized thorite previously formed under hydrothermal conditions, breaks down into huttonite at 1400°C or above.* Once formed, huttonite has never been converted into the tetragonal modification either by dry heating at lower temperatures for several days, or by prolonged treatment under hydrothermal conditions. At 1175°C and below, the 1:1 ThO_2 : SiO_2 gel yielded thorite under all water pressures. The presence of “seed” crystals had no effect on the above reactions.

From the gel starting materials ZTS 18, 19, 20, 21, 112, 134, 314 and 538 (see Table 2) whose compositions all lie on the join zircon–thorite, huttonite was formed together with zircon (and in some cases, thorite) as low as 300°C under hydrothermal conditions. The composition ZTS 19 yielded only huttonite as low as 500°C , although at 300°C both modifications were present. At face value this would suggest that the addition of ZrSiO_4 in solid solutions lowers the hypothetical thorite–huttonite transition temperature several hundred degrees; however, a considerable amount of ZrSiO_4 would then be expected in solid solution in the high form. Even at the highest temperatures (dry at 1400°C) the X-ray diffraction spacings of huttonite showed no appreciable shift. It must therefore be concluded that the formation of huttonite at “low” temperatures is not due to the lowering of the thorite–huttonite inversion temperature but merely to the effect of Zr^{4+} on the rate phenomena.

It is also necessary to consider the possibility that some thorite formed while the charge was being heated, and only partially converted to the “stable” huttonite form. This is improbable since pre-formed thorite showed no tendency to invert to huttonite even after prolonged hydrothermal treatment below 1000°C .

In an attempt to obtain equilibrium at lower temperatures, thorite, huttonite and the ThSiO_4 gel starting material were heated in molten LiF for 18 hr at approximately 900°C ; only ThO_2 could be detected in the X-ray diffraction pattern of the product. Apparently the silica did not crystallize. These data suggest the possibility that at low temperatures $\text{ThO}_2 + \text{SiO}_2$ is the stable assemblage in this binary system. A consideration of the densities of huttonite (7.0 g/cm^3),

thorite (5.3 g/cm^3) and a 1:1 molar assemblage of quartz + ThO_2 , (6.85 g/cm^3) lends some support to this hypothesis. A gel having the ThSiO_4 composition would be expected to have a statistical distribution of thorium and silicon "ions" in an oxygen-hydroxyl-water matrix, in which the Th:Si ratio is approximately 1:1 throughout. It is possible that even under hydrothermal conditions equilibrium is not reached and the gel crystallizes to the least dense assemblage, thorite. The distribution of Th and Si in the gel is closer to that of thorite than it would be to the $\text{ThO}_2 + \text{SiO}_2$ assemblage, and would therefore lead to the formation of thorite from the gels, rather than the two oxides. The latter, possibly more stable, mixture has only been produced in the extremely reactive environment of molten LiF. Opposing the above hypothesis is the fact that amorphous metamict material of supposed ThSiO_4 composition often recrystallizes to silica + thorite when heated to about 1000°C .

Owing to the enormous density difference between thorite and huttonite it was thought that this inversion would be strongly pressure dependent and have a negative slope to the p - t curve if thorite were the low-temperature form. For this reason thorite, huttonite and TS11 gel mixture were heated in the presence of water to 700°C under $150,000 \text{ lb/in}^2$ pressure for 4 days. Huttonite and thorite remained unchanged by this treatment, and the gel yielded thorite.*

It is well known that almost every natural thorite sample is partially or completely metamict indicating that perhaps there is an inherent instability to the tetragonal structure towards nuclear radiation and particle bombardment. On the other hand, a few metamict thorite specimens have rather well defined external tetragonal symmetry which supports the hypothesis that ThSiO_4 originally crystallized as thorite. Still other metamict thorites are completely formless and it cannot be said with any confidence whether or not they were first thorite or huttonite.

From the above data four separate hypotheses concerning the stability relations of ThSiO_4 are conceivable.

(1) It is reasonable that huttonite be the low temperature form of ThSiO_4 , inverting to thorite at higher temperatures. However, despite the fact that this hypothesis reconciles the densities of thorite and huttonite, the dry and hydrothermal data of this experiment prove unequivocally that huttonite is the stable form of ThSiO_4 at liquidus temperatures and persists at least as low as 1200°C .

(2) A second theory involves a lower stability limit for either of the two forms of ThSiO_4 , below which only $\text{ThO}_2 + \text{SiO}_2$ are in stable equilibrium. The results of LiF fluxing of both thorite and huttonite and the possibility of structural control during the crystallization of the gel mixtures in the hydrothermal environments of these experiments support this theory, although the relation between the two polymorphs of ThSiO_4 is still left unexplained. It is not outside the realm of possibility that the two oxides are the stable assemblage to, say, 1100°C , above which huttonite is the only stable orthosilicate. This theory must relegate thorite to a metastable role at all temperatures.

(3) The third hypothesis is what might be termed the "normal" situation in

* Note added in proof; Huttonite has been made from gels as low as 200°C and from thorite as low as 500°C by "grinding" at pressures of 20,000 to 40,000 atm. (see HOFFER and ROY, *Amer. Min.* (in press))

that thorite is the stable polymorph of ThSiO_4 up to about 1200°C above which huttonite is stable. Many of the experimental data do not support this theory and have been presented above. The facts that huttonite has been formed as low as 300°C in the binary system ZrSiO_4 – ThSiO_4 , and that huttonite has not been converted to the tetragonal polymorph cannot be reconciled with this theory. On the other hand, huttonite has been found only in one locality (PABST and HUTTON, 1951) while thorite (that is amorphous ThSiO_4 having external tetragonal symmetry) is relatively common in nature. The conversion of GdPO_4 from a monoclinic form to a “tetragonal”, thorite-like modification at low temperatures was effected experimentally in this study and supports this hypothesis. (See also the work of MOONEY (1948, 1950)).

(4) Still a fourth explanation, favoured by the writers, of the ThSiO_4 polymorphism envisages huttonite as the stable modification at all temperatures and pressures. The density relation between huttonite and a “metastable” thorite is therefore not anomalous. The formation of huttonite at low temperatures from compositions other than TS11 in the system ZrO_2 – ThO_2 – SiO_2 supports this theory. The relatively widespread occurrence of thorite in nature may be explained by the ease with which a 1 : 1 ThO_2 : SiO_2 gel or solution could possibly crystallize into the least dense assemblage, thorite. This might possibly also account for the facility with which thorite becomes metamict.*

It is obvious that the natural huttonite of PABST and HUTTON (1951) must have crystallized at temperatures below 1000°C . Dr. B. MASON (personal communication) reports a tentative second occurrence of huttonite from low-temperature hydrothermal veins of south-eastern Pennsylvania. Although huttonite is rare compared with thorite, the metastable formation and persistence of many phases is not uncommon in natural environments. Indeed, it appears that earth scientists must begin to accept the idea that a large fraction of natural assemblages are not equilibrium assemblages.

The synthesis of so-called thorogummmites, the thorium analogues of the hydroxyzircon series, also reported by FRONDEL *et al.* (1954), could not be achieved in this study. The results of the present work show that above 400°C , under hydrothermal conditions, the ThSiO_4 gel composition yielded well crystallized thorite, while those compositions richer in thoria gave both thorite plus ThO_2 . In this respect the results were quite analogous to those in the “hydrous zircon” study. However, one or two runs below 250°C appear to have only thorite present, the d -spacings of which are slightly expanded. This may possibly be due to a solid solution between ThSiO_4 and “something” which increases the unit cell volume, similar to the results of FRONDEL and COLLETTE (1957) at low temperatures. Also plotted in Fig. 2 are the molar compositions of some twenty-six thorites from the literature. It can be seen that the “thorogummmites” like the “cyrtolites” are a solid solution series between ThSiO_4 and molecular water.

* Roy (to be published) has postulated that the conditions necessary for metamictization require both the same general crystal chemical requirements as “glass-forming”, coupled with a structural limitation to those structures with a large enough hole to permit the lodgment of the displaced ions. Experiments with some forty substances, bombarded with up to 10^{20} n.v.t. total neutron flux, appear so far to confirm this hypothesis.

The system $\text{ZrO}_2\text{--ThO}_2\text{--SiO}_2$

At first glance the system $\text{ZrO}_2\text{--ThO}_2\text{--SiO}_2$ (neglecting the H_2O component since it does not appear to form a stable phase in this system) appears comparatively simple with only the phase boundaries emanating from zircon and thorite to be determined, along with the extent of solid solution between these two phases. As will be discussed below, it has been extremely difficult to establish both the stable limits of solid solution and which of the two possible tie lines, $\text{ZrO}_2\text{--ThSiO}_4$ or $\text{ThO}_2\text{--ZrSiO}_4$ is stable.

From dry runs at 1400°C and from hydrothermal runs made up to 1175°C , only very limited stable solid solution has been found between zircon and either thorite or huttonite. A review of the data compiled from spacing shifts of X-ray

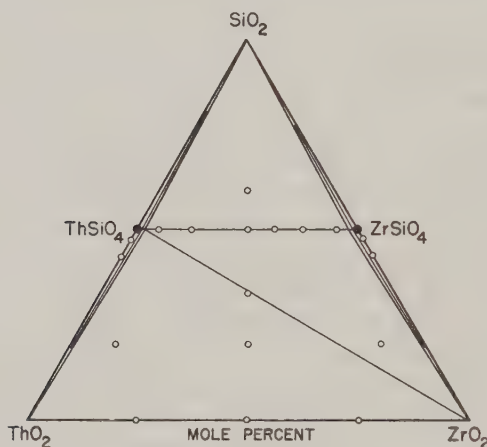


Fig. 3 The system $\text{ZrO}_2\text{--ThO}_2\text{--SiO}_2$ at subsolidus temperatures (300° to 1400°C). The small open circles in this and in the following diagrams indicate compositions which have been studied. The amounts of ZrSiO_4 and ThSiO_4 in thorite and zircon (6 ± 2 and 4 ± 2 moles per cent, respectively) are slightly exaggerated for visual clarity.

diffraction peaks reveals that less than 4 ± 2 moles per cent ThSiO_4 dissolves in zircon and no more than 6 ± 2 moles per cent ZrSiO_4 in either thorite or huttonite at the highest temperatures studied. Due to the inconsistency of many of the data and the metastability problem (*vide infra*) it has been impossible to establish firmly any relation between the amount of solid solution and either temperature or pressure, although thermodynamic considerations require that the amount of solid solution vary with both.

In Fig. 3 are shown the three-phase assemblages and stable tie lines in the system $\text{ZrO}_2\text{--ThO}_2\text{--SiO}_2$. The limits of solid solution between zircon and ThSiO_4 are slightly exaggerated for visual clarity. The system $\text{ZrO}_2\text{--ThO}_2$ is discussed by the writers elsewhere (MUMPTON and ROY, 1960).

The connode $\text{ZrSiO}_4\text{--ThSiO}_4$ has been firmly established from runs made with compositions lying along the zircon-thorite join, from which only zircon and either thorite or huttonite were formed. In some of the runs from these mixtures the diffraction pattern of ThO_2 was observed, indicating that the sealed

gold tube had burst during the run, and that silica had been leached from the charge.

The evidence indicating which of the joins, $\text{ZrSiO}_4\text{-ThO}_2$ or $\text{ThSiO}_4\text{-ZrO}_2$, represents the stable conjugate pair of phases is not nearly so conclusive. The runs listed in Table 3 from compositions ZTS 111, 221, 172, and 712 give conflicting results in many cases. At higher temperatures (above 1200°C) there is little

Table 3. Abstract of experimental results*

Run	Temperature ($^\circ\text{C}$)	Pressure (lb/in ^{2})	Duration (days)	Products and remarks
<i>Composition ZS 11</i>				
137	200	20,000	22	Zircon (poorly crystallized)
531	250	40,000	44	Zircon (well crystallized)
586	1500	dry	3	Zircon (well crystallized)
705†	1500	dry	3	Zircon (well crystallized)
<i>Composition ZS 1-90</i>				
138	200	20,000	22	Zircon (poorly crystallized) + some ZrO_2
522	250	40,000	44	Zircon (well crystallized) + ZrO_2
86	1450	dry	2	Zircon (well crystallized) + some ZrO_2
<i>Composition ZS 1-75</i>				
139	200	20,000	22	Zircon (poorly crystallized) + some ZrO_2
523	250	40,000	44	Zircon (well crystallized) + some ZrO_2
231	900	6000	12	Zircon (well crystallized) + some ZrO_2

* Table 3 is an abstract indicating the type of data obtained. A full summary listing the details of all runs is available from the University Microfilms, Ann Arbor, Michigan.

† Starting material was product from run 254.

doubt that ThSiO_4 and ZrO_2 are stable together and the Alkemade triangles consist of $\text{SiO}_2 + \text{ThSiO}_4 + \text{ZrSiO}_4$ and $\text{ZrO}_2 + \text{ZrSiO}_4 + \text{ThSiO}_4$, and $\text{ThSiO}_4 + \text{ThO}_2 + \text{ZrO}_2$. Additional support for this tieline comes from the fact that although the products of run 508 (made from composition ZTS 111 at 800°C and 25,000 lb/in ^{2}) consisted of zircon + ThO_2 , after additional heating at 1400°C dry (run 564), this material reacted to form huttonite + ZrO_2 (plus remnant zircon and ThO_2).

At lower temperatures, however, the data are much more equivocal. The products of several runs from compositions ZTS 111 and 712 appear to support the opposite tieline, zircon + ThO_2 . A consideration of the densities of the various phase assemblages suggests some explanation of these data. Considering the join zircon- ThO_2 , a 1:1 molar ratio mixture has a density of 6.75 g/cm ^{3} , while a 1:1 molar ratio with $\text{ThSiO}_4\text{-ZrO}_2$ yields a density of 6.65 g/cm ^{3} if huttonite is used, and 5.37 g/cm ^{3} when thorite is used. From volume considerations the similarity in the densities of 1:1 mixtures on these two cross joins gives rise to the possibility that one pair of conjugate phases may form metastably and persist over a wide range of temperatures. It is likely that the phase assemblages giving rise to the join zircon- ThO_2 at lower temperatures are metastable with respect to those which indicate the stable tieline $\text{ThSiO}_4\text{-ZrO}_2$.

One cannot, however, overlook the possibility that a crossed relation might exist between these two pairs of conjugate phases with a possible reaction taking place at about $1000^{\circ}\text{C} \pm 100^{\circ}\text{C}$ or even lower. Natural occurrences of thorianite, most likely having crystallized well below 1000°C support the tieline zircon- ThO_2 , among which is the thorianite from Easton, Pennsylvania (see WELLS *et al.*, 1933) although the thorianite in this case contains at least 50 per cent UO_2 . These occur as black crystals encased in larger masses of zircon and allanite. The fact that natural baddeleyite has never been reported in association with thorite might

Table 4. X-ray diffraction spacings of products*
(Zircon in the system $\text{ZrO}_2\text{-ThO}_2\text{-SiO}_2$)

Run	Composition	$2\theta_{(200)}$	ThSiO_4 (moles %)
115	ZTS 112	26.350	33
117	ZTS 314	26.450	28
118	ZTS 538	26.282	36
123	ZS 1.90	26.995	0
129	ZTS 538	26.422	28
171	ZTS 112	26.266	37
172	ZTS 134	26.603	20
173	ZTS 314	26.229	39
205	ZTS 314	26.949	3
206	ZTS 538	26.928	3
391	ZTS 314	26.882	6
405	ZTS 112	26.918	5
408	ZTS 538	26.938	3
432	ZTS 134	26.846	8
435	ZTS 112	26.288	36
436	ZTS 134	26.321	35
437	ZTS 314	26.394	30
438	ZTS 538	26.381	32
455	ZTS 314	26.494	25
456	ZTS 112	26.965	2
458	ZTS 314	26.941	3
651	ZTS 112	26.921	4
652	ZTS 134	26.967	2
653	ZTS 314	26.983	1
654	ZTS 538	26.937	3

* Similar plots showing zircon in the system $\text{ZrO}_2\text{-UO}_2\text{-SiO}_2$, thorite in the system $\text{ThO}_2\text{-ZrO}_2\text{-SiO}_2$, thorite in the system $\text{ThO}_2\text{-UO}_2\text{-SiO}_2$, baddeleyite in the system $\text{ZrO}_2\text{-ThO}_2\text{-SiO}_2$, baddeleyite in the system $\text{ZrO}_2\text{-UO}_2\text{-SiO}_2$, thorianite in the system $\text{ZrO}_2\text{-ThO}_2\text{-SiO}_2$, thorianite and uraninite in the system $\text{ThO}_2\text{-UO}_2\text{-SiO}_2$, and uraninite in the system $\text{ZrO}_2\text{-UO}_2\text{-SiO}_2$ are available from the University Microfilms, Ann Arbor, Michigan.

also be used as evidence in support of the zircon- ThO_2 tieline at least at lower temperatures.

One of the most constant features and headaches of this work has been the finding of surprisingly persistent metastable equilibria among these tetravalent oxides and silicates. In numerous runs it has been possible to prepare metastable solid solutions between zircon and thorite which extend almost to 35 moles per

cent ThSiO_4 in zircon and to about 25 moles per cent ZrSiO_4 in thorite. These materials readily exsolve when reheated at higher temperatures under pressure to the above-mentioned solid solution limits. A complete metastable series of solid solutions between thorite and zirconia has also been observed and is discussed elsewhere by the writers (MUMPTON and ROY, 1960).

The effect of UO_2 additions

The substitution of uranium for zirconium and thorium in zircon, thorite, thorianite and baddeleyite is an important concept both from the point of view of crystal chemistry as well as for the interpretation of natural assemblages of these minerals coexisting with uraninite. The best attack on this problem is an experimental determination of the quaternary system $\text{ZrO}_2\text{--ThO}_2\text{--UO}_2\text{--SiO}_2$, but since none of the ternary systems and even a few of the binary systems have not been studied up to this time, it has been necessary to limit the present investigation to preliminary studies in the subsolidus portions of the systems $\text{ZrO}_2\text{--UO}_2\text{--SiO}_2$ and $\text{ThO}_2\text{--UO}_2\text{--SiO}_2$, dealing directly with the zirconthorite group. (Results on the systems $\text{ZrO}_2\text{--UO}_2$ and $\text{ThO}_2\text{--UO}_2$ are reported elsewhere by the authors, (MUMPTON and ROY, 1960).

The addition of uranium oxide to systems involving thorite, zirconia and silica imposes additional "valence state" phenomena on the already present metastability problem. Since the phase equilibria among these uranium compounds cannot be exactly determined without first the knowledge of the equilibria in the systems U--O , U--Zr--O and U--Th--O , etc., the present results are of necessity only preliminary. This study is therefore aimed only at answering a few specific questions.

Data indicating the limits of solid solutions of " USiO_4 " in zircon and thorite and of UO_2 in thorianite and baddeleyite have been determined and not-impossible compatibility triangles are presented for the ternary systems in which UO_2 is a component. The system $\text{UO}_2\text{--SiO}_2$ contains no compounds and several dozen attempts at the synthesis of " USiO_4 " have consistently failed. The mineral coffinite has been reported to be a hydroxylated variety of " USiO_4 ", (see STEIFF *et al.*, 1956), much like the so-called cyrtolite and thorogummite series discussed earlier, and its synthesis is briefly discussed by HOEKSTRA and FUCHS (1956). The results of the present study show that a coffinite-like compound cannot be synthesized reproducibly in the presence of water. It is therefore safe to assume that no *stable* binary compounds exist in the binary system.

Of primary interest to the mineralogy of zircons and thorites are the limits of solid solution between ZrSiO_4 , ThSiO_4 and the hypothetical compound " USiO_4 ". Such information may be also helpful in the interpretation of age determination data.

The system $\text{ZrO}_2\text{--SiO}_2\text{--UO}_2$

In lieu of adequate data on the "redox" reactions in the system $\text{ZrO}_2\text{--UO}_2\text{--SiO}_2$ under hydrothermal conditions, the runs must be cautiously interpreted, especially if solid solution limits are desired. From the several runs made in controlled oxygen atmosphere at 1350°C , it can be seen that no more than about 4 ± 2

moles per cent of the compound "USiO₄" dissolves in zircon, and mixtures on this join gave zircon(ss) + SiO₂ + UO₂(ss) as products further confirming the non-existence of "USiO₄". Other compositions in this system run under these conditions support the 8 ± 2 moles per cent ZrO₂ solid solution limit in uraninite at 1350°C. These data indicate that the probable phase assemblages in the systems are those shown in Figure 4. Although the two-phase regions, SiO₂-zircon(ss) and ZrO₂-zircon(ss) have not been determined experimentally there is

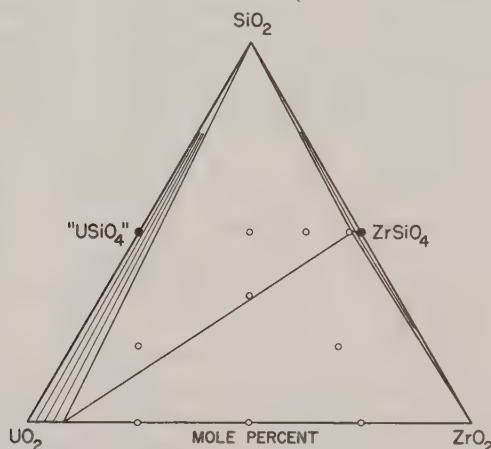


Fig. 4. The system ZrO₂-UO₂-SiO₂ at temperatures below the solidus from 300 to 1350°C. The amount of solid solution of "USiO₄" in zircon (about 4 ± 2 moles per cent) is slightly exaggerated for visual clarity.

little doubt that they exist. The Alkemade triangle SiO₂-UO₂(ss)-zircon(ss) has been drawn from the fact that all mixtures within this triangle gave cubic solid solutions of from 8 to 10 moles per cent zirconia in equilibrium with silica and the zircon solid solution.

In spite of the fact that the hydrothermal results are much more ambiguous, a consideration of the data results in a confirmation of the above solid solution limits and compatible assemblages. At the lower temperatures of the hydrothermal runs the metastability problem again enters the picture. It has been possible to prepare zircon(ss) containing up to 20 moles per cent "USiO₄" under what are most likely metastable conditions.

Contrary to the evidence reported by FRONDEL (1957, p. 4) that zircon and zirconium-free uraninite "cocrystallize" in certain pegmatites, it is apparent from the present laboratory experimental work that zircon can exist in stable equilibrium only with the uraninite solid solution containing the maximum (8 per cent) amount of zirconia. It is felt that the natural assemblage referred to above is not at equilibrium, and may be due to two generations of crystallization.

The system ThO₂-UO₂-SiO₂

Because of the difficulties encountered in the subsolidus region of the system ZrO₂-UO₂-SiO₂ and the uncertainties still remaining in the system ThO₂-UO₂, only a few runs have been made in the present system. FRONDEL (1957) has

previously reported that solid solution “... extends from ThSiO_4 towards USiO_4 up to at least 50 moles per cent USiO_4 ”, although no experimental data were given.

Runs made under partial pressure of oxygen of $10^{-9.8}$ atm at 1350°C give rise to the Alkemade triangles shown in Fig. 5. From this diagram it can be seen that a two-phase region $\text{SiO}_2\text{--UO}_2\cdot\text{ThO}_2(\text{ss})$ extends to about 67 moles per cent ThO_2 at this temperature and that only a narrow three-phase field of $\text{UO}_2\cdot\text{ThO}_2(\text{ss})\text{--ThSiO}_4(\text{ss})\text{--SiO}_2$ is stable. It can plainly be seen that ThSiO_4 does not dissolve

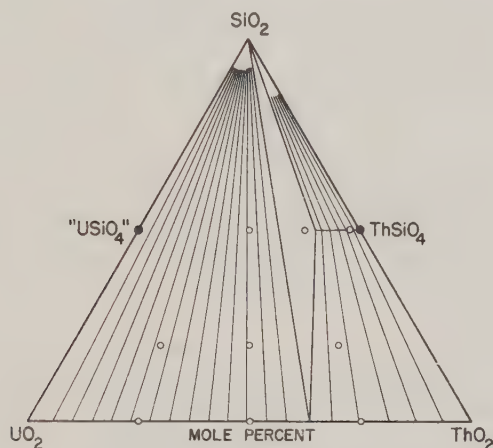


Fig. 5. Not-impossible version of the system $\text{ThO}_2\text{--UO}_2\text{--SiO}_2$ at 1350°C above the possible solvus in the system $\text{ThO}_2\text{--UO}_2$. The composition of the $\text{UO}_2\text{--ThO}_2$ solid solution in equilibrium with SiO_2 and $\text{ThSiO}_4(\text{ss})$ is not unequivocal. Tie lines are only hypothetical.

more than about 20 moles per cent “ USiO_4 ” at this temperature and that the name “uranothorite” is perhaps unjustified. An examination of the few hydrothermal runs made in the system $\text{ThO}_2\text{--UO}_2\text{--SiO}_2$ shows that definite conclusions cannot be drawn about the equilibria at temperatures below 1350°C . If a two-phase region in the system $\text{ThO}_2\text{--UO}_2$ exists at lower temperatures, a three-phase triangle, consisting of two cubic solid solutions and silica, would be expected in the ternary system. Several runs suggest this relation although partial oxidation of the charges and the absence of equilibrium may account for the discrepancies in the data.

In an attempt to produce a sufficiently low oxygen pressure in a hydrothermal run, uranium metal was added in a separate envelope to the pressure vessel. In runs at 800°C and $30,000\text{ lb/in}^2$ the metallic uranium oxidized to UO_2 , although the unit cell dimensions of this product ($a_0 = 5.546\text{ \AA}$) suggest that oxidation has proceeded slightly past stoichiometric UO_2 towards U_3O_8 . In this run each of the mixtures TU 11 and 13 yielded only a single cubic solid solution, whose cell dimensions were identical with those determined for high temperature solid solution phases within experimental error. Mixtures whose compositions lie within the ternary system, however, gave the indication that a two-phase region was present in the binary system. The inability to cope with oxidation–reduction reactions under hydrothermal conditions combined with the complexities of

metastable equilibrium restrict the value of a more thorough discussion of these data at this time.

CONCLUSIONS

Solid solution limits of zircon and thorite

The stable limits of solid solution among the silicates of zirconium, thorium and uranium have been discussed in previous sections. It is important to note that although zircon and thorite are isomorphous, the amount of ThSiO_4 soluble in zircon is limited to less than 4 moles per cent, while only 6 ± 2 moles per cent ZrSiO_4 dissolves in thorite at the highest temperatures, about 1000°C . From the absence of spacing shifts in the X-ray diffraction patterns of huttonite in equilibrium with zircon, there is apparently little if any solid solution in the monoclinic form of ThSiO_4 with zircon. The solubility of the theoretical compound " USiO_4 " is somewhat more extensive and reaches a stable limit of about 20 moles per cent in ThSiO_4 and 4 ± 2 moles per cent in zircon. Since the solid solution in either case does not approach 50 moles per cent there seems little justification for calling some uranium-containing thorites, "uranothorites" and the chemical taxonomy of minerals in recent years suggests that such phases be designated as uranoanthorites or uranoan-zircons.

Between thorite and zircon it has been possible to prepare metastable solid solutions containing up to 25 and 35 moles per cent ZrSiO_4 and ThSiO_4 in thorite and zircon, respectively. Under no conditions has complete solubility been observed between these two compounds. The metastable solubility limits between ZrSiO_4 and " USiO_4 " and between ThSiO_4 and " USiO_4 " have not been specifically determined although zircons and thorites have been prepared containing about 20 and 30 moles per cent " USiO_4 ". At higher temperatures these metastable products evolve to the stable solid solution limits.

The analyses of natural thorites and zircons are also inadequate for a detailed interpretation. On the whole, from some ninety analyses of zircon and thorite in the literature, the following limits of solubility are suggested from the literature.

Zircon, less than 1 mole per cent ThSiO_4 ;
less than 5 moles per cent " USiO_4 ."

Thorite, less than 10 moles per cent ZrSiO_4 ;
less than 35 moles per cent " USiO_4 " although most
samples contain less than 5 moles per cent.

A considerable number of zircon analyses list significant amounts of yttrium, cerium, niobium, etc. Disregarding the possibility that these elements may only be present as impurities, important solid solution series do exist between ZrSiO_4 and several trivalent phosphates. It is entirely likely that niobium and tantalum enter the zircon lattice accompanied by a trivalent element such as iron (or yttrium) which compensate for the charge difference between Nb^{5+} and Zr^{4+} .

Geologic significance

As is the case with most studies of binary and ternary systems, the experimental results do not by themselves solve specific geologic problems, but must

serve as a basis for future work in more complicated systems. Many concrete conclusions may be drawn, however, from the data of the present work and may serve to clarify some of the paragenetic relations of deposits of zircon, thorite, thorianite and uraninite.

From the system $\text{ZrO}_2\text{--UO}_2\text{--SiO}_2$ the stable three-phase assemblages are $\text{SiO}_2\text{--UO}_2(\text{ss})\text{--zircon}(\text{ss})$ and $\text{UO}_2(\text{ss})\text{--zircon}(\text{ss})\text{--ZrO}_2(\text{ss})$. If zircon(ss) and uraninite(ss) are in equilibrium with either quartz or baddeleyite, each must contain the maximum amount of solid solution with “ USiO_4 ” and ZrO_2 , respectively.

In the system $\text{ThO}_2\text{--UO}_2\text{--SiO}_2$ it can be seen that above a possible solvus in the binary $\text{UO}_2\text{--ThO}_2$, in the presence of quartz, thorite(ss) can coexist only with those members of the $\text{UO}_2\text{--ThO}_2$ solid solution series which are rich in thorium. Pure uraninite and thorite are incompatible at these temperatures, and even below the possible solvus.

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An example of variation in constituents of hot springs

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Abstract—A consideration of the observed results obtained at Misasa Hot Springs, Japan, has led to the following conclusions: when a factor acts continuously on the hot spring, the frequency distribution of the observed values for each constituent is normal, but the combined effect of several factors may cause the frequency distributions to be non-normal. Then, the extent of the effect caused by a given factor might be determined by the test for non-normality of the frequency distribution of observed values with respect to that factor.

INTRODUCTION

It is commonly known that the constituents of hot springs vary and, up to the present, many results have been reported on the variation of these constituents. These results have been considered from several points of view by other authors, and many varying conclusions have been reached.

As a new consideration, the frequency histograms for the observed values obtained in Misasa Hot Springs, Tottori-ken, Japan were prepared, and the relation between the factors which act on the springs and the frequency histograms are discussed.

DATA USED AND ITS TREATMENT

The location of Misasa Hot Springs is shown in Fig. 1. Although there are about one hundred springs, only *main* springs and those on which data are treated here, are plotted in Fig. 1.

Continuous observations were made on "Hisui-no-Yu" (orifice) from April, 1951 to March, 1952 (UMEMOTO, 1952), and on the other springs from May, 1952 to April, 1953 (SUGIHARA, 1956). The data obtained by these observations are used.

"Hisui-no-Yu" (orifice) was observed almost every day from April 27, 1951 to July 10, twice weekly from mid-July to the end of December, and once a week thereafter. Then the values for one day were taken at random from the values for each week during the first period from April 27 to December, and these one-day values were collated with the values during the second period. The frequency histograms for each constituent were prepared from these data.

In the rainy season from mid-June to early-July, the rice-fields surrounding these hot springs are irrigated and by mid-September are flooded. The ground water level is considerably higher during this period compared with the rest of the year. From the beginning of this season, sudden changes are observed on "Hisui-no-Yu" (orifice). The water temperature rises, the rate of flow increases, the chloride and sulphate content decreases, and the radon content increases. When the water is drained from the rice-fields in mid-September the changes are reversed. These changes are sudden and discontinuous, and at other times of the year the changes are not so marked. For this reason, two series of frequency histograms were prepared based on the observed values for the irrigation and non-irrigation season. In comparison with the number of samples taken during the

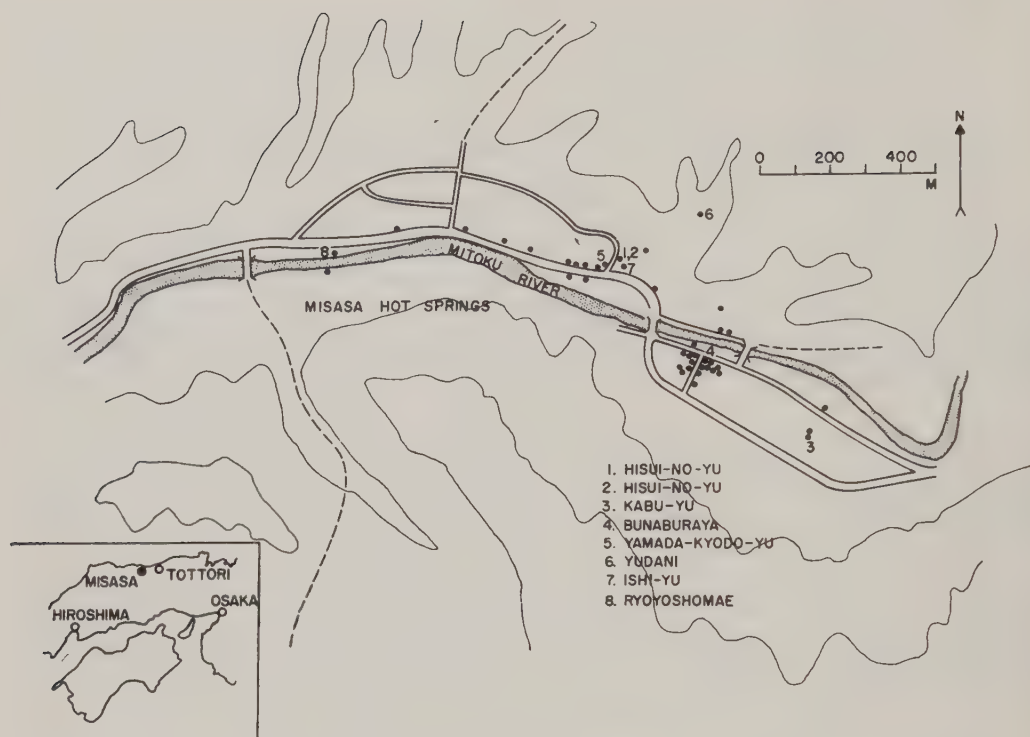


Fig. 1. Misasa Hot Springs.

non-irrigation season, those of the irrigation season were relatively large because the observations were made twice a week throughout this latter season.

The other springs were observed twice a week. The data which were satisfactory enough to be treated were taken from the results on these springs, and the frequency histograms for each measurement made on these over a period of one year, were prepared as in the case of "Hisui-no-Yu" (orifice).

The constituents of many springs are known to change in the irrigation season in a manner similar to those of "Hisui-no-Yu" (orifice). Based on the observed values of these, two series of frequency histograms were prepared for the irrigation season and non-irrigation season.

The test for non-normality of frequency distribution was made by the χ^2 -test.

In the preparation of histograms, several values, which seemed to be in error, because of their extreme extraordinariness, were omitted.

RESULTS

"Hisui-no-Yu" (orifice)

The results of the test are shown in Table 1, in which "normal" indicates the denial of the assumed non-normality and "non" the non-denial. Several representative frequency histograms are shown in Figs. 2 to 5. In the case of denial of the assumed non-normality, the expected normal distribution curves are also shown.

Table 1. Results of the χ^2 -test for non-normality of the observed values on "Hisui-no-Yu" (orifice)

	Full year period		Non-irrigation season		Irrigation season	
	Normality	Number of samples	Normality	Number of samples	Normality	Number of samples
Rate of flow	normal	43	normal	31	normal	27
Water temperature	normal	43	normal	31	normal	27
Cl ⁻ content	non	43	normal	31	normal	27
SO ₄ ²⁻ content	non	42	normal	30	normal	27
HCO ₃ ⁻ content	normal	42	normal	29	normal	27
Rn content	non	40	non	28	normal	27
Ra content	normal	41	normal	29	normal	27
NH ₄ ⁺ content	normal	38	normal	27	normal	25

The observed values of each constituent during a year are not always distributed normally, but when the values are divided into two series of values obtained in a vigorously changed period and in the other times of the year the two series of values are distributed normally except those of radon.

Other springs

The results of the tests for non-normality for a year are shown in Table 2. It seems that the values of each constituent do not always distribute normally.

Among these springs, "Kabu-Yu", "Yamada-kyodo-Yu", "Hisui-no-Yu" (bathtub), and "Ishi-Yu" are seriously affected by the irrigation of the rice-fields. The observed values of each constituent of these four springs were tested for non-normality of their frequency histograms in the irrigation and non-irrigation seasons. The results are shown in Tables 3 and 4. These results are not in accordance with the results of "Hisui-no-Yu" (orifice) and it cannot be seen that all observed values of all constituents distribute normally.

DISCUSSION

Many factors are known to affect the constituents of hot springs. These are temperature, atmospheric pressure, rainfall, snowfall, volcanic activity, the ground water level, the water level of nearby rivers, the ebb and flow of the oceans, etc. Misasa Hot Springs seem to be affected by a complicated combination of these sources of variations except volcanic activity and the ebb and flow of the ocean. Each spring seems to be affected in a different degree by each factor.

In "Hisui-no-Yu" (orifice), when the effects of a main source of variation which acts seriously and discontinuously on the hot spring are eliminated, i.e. when each source of variation which acts continuously on the hot spring is combined linearly together, all frequency histograms of its observed values for each constituent are found to be normal. Hence, the observed values caused by a continuous source of variation seem to distribute normally and their linear combination also seems to distribute normally. In addition to the variation in the

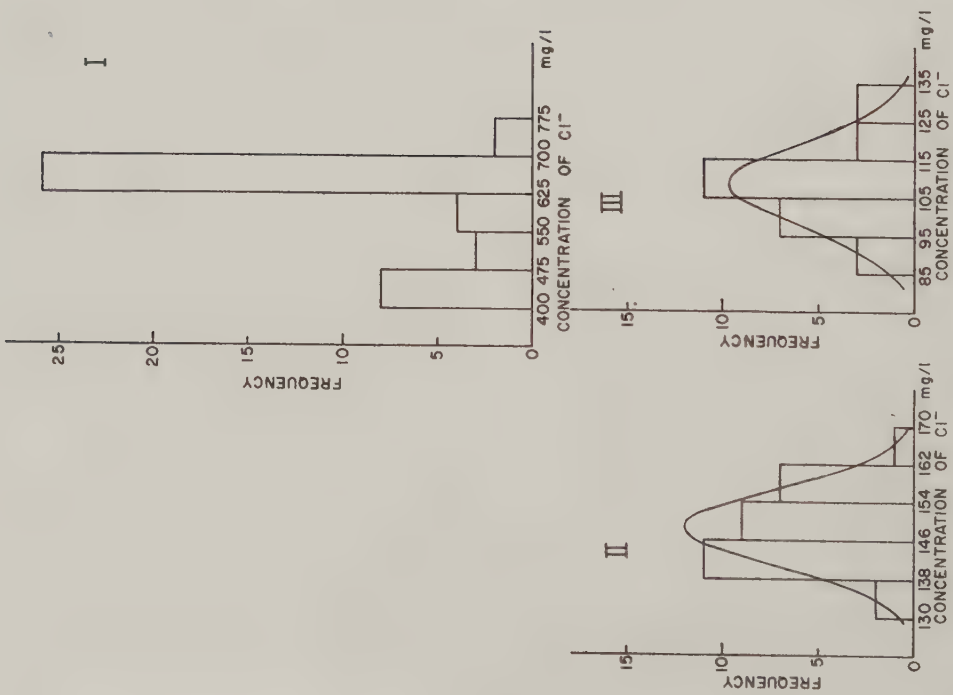


Fig. 2. Frequency histograms of Cl^- content of "Hisui-no-Yu" (orifice)
I: A full year period II: Non-irrigation season III: Irrigation season

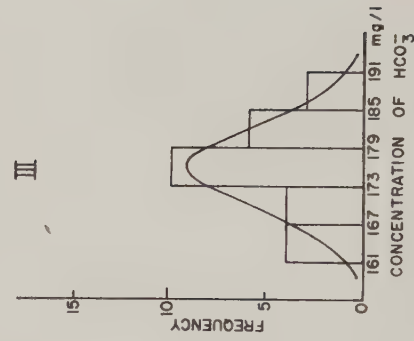
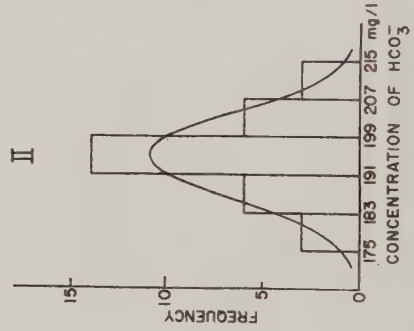
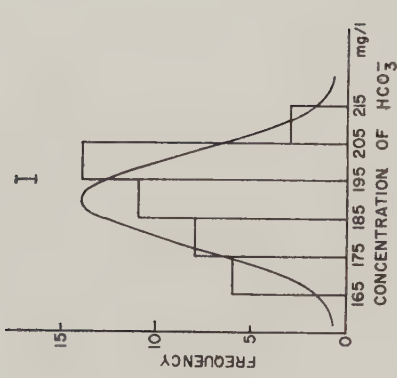


Fig. 3. Frequency histograms of HCO_3^- content of "Hisui-no-Yu" (orifice)
I, II, and III are the same as in Fig. 2.

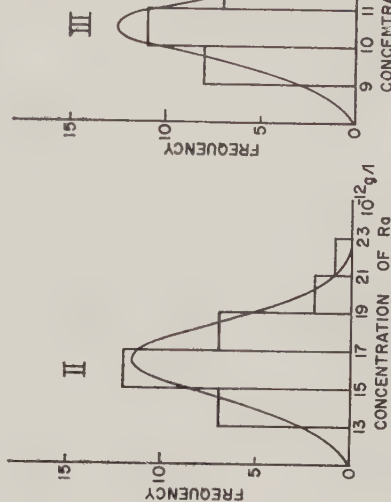
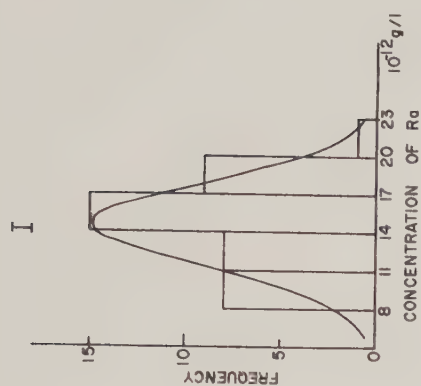


Fig. 5. Frequency histograms of Ra content of "Hisui-no-Yu" (orifice)
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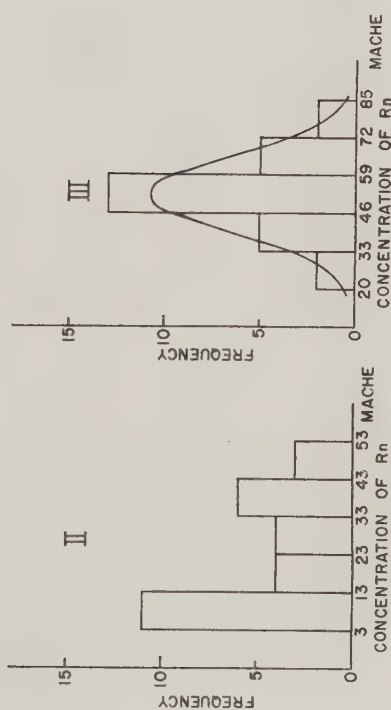
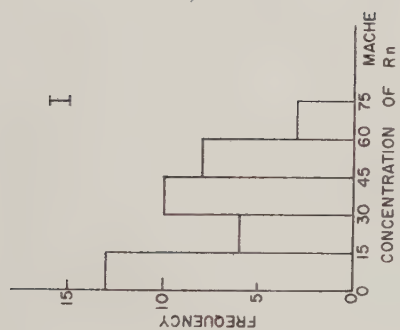


Fig. 4. Frequency histograms of Rn content of "Hisui-no-Yu" (orifice)
I, II, and III are the same as in Fig. 2.

Table 2. Results of the χ^2 -test for non-normality of the observed values on the other springs during a full year

	Kabu-Yu		Bunaburaya		Yamada-kyodo-Yu		Hisui-no-Yu (bathtub)		Yudani		Ishi-Yu		Ryoyoshomae	
	Nor-mality	Number of samples	Nor-mality	Number of samples	Nor-mality	Number of samples	Nor-mality	Number of samples	Nor-mality	Number of samples	Nor-mality	Number of samples	Nor-mality	Number of samples
Rate of flow	—	—	—	—	—	—	—	—	—	—	—	—	non	101
Water temperature	normal	101	non	98	non	96	normal	108	non	90	non	102	non	104
Cl ⁻ content	normal	99	normal	101	non	96	non	108	normal	92	non	103	non	103
HCO ₃ ⁻ content	non	101	non	100	normal	95	non	107	non	91	normal	103	non	104
Rn content	non	101	normal	100	non	96	normal	110	normal	91	normal	103	non	104
Mg ²⁺ content	normal	101	non	100	non	95	non	107	normal	91	normal	103	non	104

Table 3. Results of the χ^2 -test for non-normality of the observed values on the several springs during the non-irrigation season

	Kabu-Yu		Yamada-kyodo-Yu		Hisui-no-Yu (bathtub)		Ishi-Yu	
	Nor-mality	Number of samples	Nor-mality	Number of samples	Nor-mality	Number of samples	Nor-mality	Number of samples
Water temperature	non	75	non	66	normal	81	non	76
Cl ⁻ content	normal	74	non	66	non	82	normal	76
HCO ₃ ⁻ content	non	75	normal	66	normal	82	normal	76
Rn content	normal	72	normal	64	normal	83	normal	76
Mg ²⁺ content	normal	75	normal	65	normal	81	normal	76

water level of the rice-fields, there seems to be a factor which acts discontinuously on the radon content of this spring, and the radon content may vary in accord with the effect of such a factor. The abrupt and temporary variation in radon content in the other mineral springs has been reported (IWASAKI, 1943; KURODA, 1943; GENSER, 1923) and in Misasa the same variation was also found (ASHIZAWA, 1950). At "Hisui-no-Yu" (orifice), such variation seems to occur although it is not apparent in the data used.

Table 4. Results of the χ^2 -test for non-normality of the observed values on the several springs during the irrigation season

	Kabu-Yu		Yamada-kyodo-Yu		Hisui-no-Yu (bathtub)		Ishi-Yu	
	Nor-mality	Number of samples	Nor-mality	Number of samples	Nor-mality	Number of samples	Nor-mality	Number of samples
Water temperature	normal	26	non	26	normal	27	non	25
Cl ⁻ content	normal	25	normal	26	non	24	normal	26
HCO ₃ ⁻ content	normal	26	normal	25	normal	25	normal	26
Rn content	normal	26	normal	26	normal	27	normal	26
Mg ²⁺ content	normal	26	non	26	normal	26	normal	26

In the springs other than "Hisui-no-Yu" (orifice), the observed values for a full year do not always distribute normally. As for the observed values of the springs which are known to be affected by the water level of the rice-fields, the number of the normally distributed constituents in the non-irrigation season is greater than for a full year period, and the number in the irrigation season is still greater than in the non-irrigation season. This tendency is similar to but not quite the same as that of "Hisui-no-Yu" (orifice). The inverse tendency is found in the water temperature variation of "Kabu-Yu". Usually, atmospheric temperature has an effect on water temperature. In this spring, the water temperature drops and the rate of flow decreases in the non-irrigation season; then the decrease of water temperature seems to be accelerated, i.e. interaction appears.

By the elimination of the effects induced by the sources of variation which are

discontinuous and highly variable, the frequency histograms of the values tend to be normal. Although the histograms are apt to be normal under the effect of each source of variation which acts continuously, as a whole, the values do not always distribute normally when a complicated combination of the sources act together.

When the selection of the factor is not proper as in the case of the water temperature of "Kabu-Yu", the results of the partitioning of the observed values are quite different from the above-mentioned results, because a factor having an effect on one of the constituents of hot springs does not necessarily act in the same manner on all constituents.

By the treatment of the data of other springs in Misasa, one should be able to investigate the extent of the effects by various factors, but it is impossible to treat the data with respect to the factors which are considered to have an effect, because of the lack of data on such factors. For example, the spring "Ryoyoshomae" issues from very near the river bank and the water level of the river must be one of the main sources of variation, but the water level has not been recorded.

The data used here has been obtained for only one year and the number of samples is small. The usage of data obtained in a longer period will be more significant, but the treatment of such data will be more difficult because of a newly introduced factor, the drilling of new springs.

It is known that even if the non-normality of the distribution of a large number of samples extracted from a group was affirmed, that of a small number of samples extracted from the same group may be denied. Therefore, the conclusions in the present discussion are somewhat limited by the above conditions, but such a tendency is conceivable.

CONCLUSION

Each usual source of variation acting on a constituent of the hot springs studied, varies the constituent so that its frequency histogram may distribute normally, but the frequency histogram of observed values for the constituents do not always appear normal under the action of a combination of these sources and other unusual sources.

If the test for non-normality of the frequency histogram of a constituent is made after the proper treatment of data with respect to a source of variation, it may be possible to ascertain the extent of the effect induced by the source, on the constituent.

In general, an analysis table is used to represent the constituent of a hot spring. It seems to be desirable, however, to use the analysis table which is prepared from observation on the sources of variation acting on the spring.

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Deuterium content of minerals, rocks and liquid inclusion from rocks

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Abstract—Samples of some minerals, rocks and liquid inclusions from rocks have been analysed for water and deuterium content of the water. Samples from Hawaii and Japan were selected with the prime objective of securing juvenile water. It is found that the water of these samples contains *less* deuterium than the average surface water of the earth, and it is concluded that juvenile water does not contain as much deuterium as the oceans. Possible explanations for the discrepancy are offered. (1) Protium equivalent to about 4 per cent of the oceans has escaped from the earth with a negligible loss of deuterium. (2) The earth at its formation acquired surface water of high deuterium content and deeply buried water of low deuterium content. It is pointed out that certain carbonaceous chondrites contain the highest concentrations of deuterium ever found in Nature, while others of this group contain water of about average terrestrial composition. Other samples of water have been analysed and are reported even though the results do not contribute to the main problem. The results do not differ in any important way from others reported in the literature.

INTRODUCTION

RUBEY (1951) has presented very impressive evidence supporting the view that the oceans have been produced from the earth's interior by the escape of water through volcanoes and hot springs. It is evident that such water should have the isotopic composition of the mean surface water and this conclusion could be confirmed if reliable samples of juvenile water are secured and analysed for deuterium. The analysis for oxygen-18 is not possible because methods of extracting water from samples will probably lead to unknown exchange of the oxygen isotopes between the water samples and the oxygen of the silicates.

Samples of water from igneous rocks have been analysed and the concentration of deuterium has been found to be markedly less than its concentration in sea water (BOATO, 1954; FRIEDMAN and SMITH, 1958). However, it has always been possible to ascribe the observed effect to waters which are generally low in deuterium concentration because fresh water has been fractionated by evaporation and condensation processes. Also, spring waters are mostly surface water and the amount of juvenile water, if it is present in such sources at all, is too low to be detected with certainty (CRAIG *et al.*, 1956).

We have considered that juvenile water could be secured from the Hawaiian volcanic rocks for the following reasons. At some time in the past, lava originating below the crust flowed through a fissure in the ocean floor and this lava came in contact with ocean water. Further eruptions built the Hawaiian volcanoes, always under conditions where only ocean water could be added to the rocks. Even after they extended above the ocean, the rain water which may have fallen on them has an isotopic composition near that of the ocean. Thus the Hawaiian rocks may be contaminated with water of oceanic composition, but if they contain less deuterium relative to protium than the oceans, the difference must be at least

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in part real and not due entirely to contamination. It will be shown in this paper that this is indeed the case.

Less clear is the situation with respect to rocks from Japan because the rain water contains less deuterium than ocean water and the lavas may come from remelted crustal material.

There is good evidence for the view that volcanic bombs come from the mantle in unchanged condition or from the lower parts of the crust, and hence such bombs are particularly interesting from the standpoint of the isotopic composition of their hydrogen. The water of these rocks is very strongly bound so that exchange with the surface waters after arrival at the surface is unlikely in this case.

SAMPLES

The mineral samples of North America were furnished by Dr. M. N. BASS and Dr. R. MARSHALL. The samples of rocks from Hawaii were submitted by Dr. G. A. MACDONALD. Most of the rock samples from Japan were contributed by Dr. I. IWASAKI. The water samples from Japan were supplied by Mr. Y. IDE. Other samples were collected by one of the authors (N. KOKUBU).

EXPERIMENTAL

The method of analysis of D/H ratio for minerals and rocks with a combustion technique has some similarity to that of BOATO (1954) who used it in the analysis of meteorites, but is different in many points.

The apparatus is shown in Fig. 1. The mineral or rock sample is placed in a platinum boat, *A*, and is first dried in a vacuum to 110°C, in order to drive off any moisture which might have been absorbed from the atmosphere. A certain amount of pure oxygen at reduced pressure (~50 mm Hg) is then allowed to fill the sillimanite combustion tube. The sample is heated with an electric furnace to 1100°C. The oxygen in the combustion tube is cycled by the use of an automatic Toepler pump.

The Pt catalyst in *B* is maintained at 800°C, and the silver gauze contained in the furnace, *C*, has a temperature gradient from 300 to 450°C. The condensible combustion products, water and carbon dioxide, are trapped in *T-A* with liquid nitrogen. After 1 hr heating of the sample at 1100°C, the system is then pumped to remove oxygen. The liquid nitrogen is removed and the dry ice vessel is placed to the *T-A* trap. After enough time has passed most of the carbon dioxide is pumped away. Water is then trapped in the *T-B* trap with liquid nitrogen while the *T-A* trap is warmed with hot water. When enough time has elapsed to insure complete condensation, the vacuum is checked by the thermocouple gauge (*TG*). The dry ice vessel is attached to *T-B* and after enough time has passed the remaining CO₂ is pumped out completely. Water is finally collected in sample tube *T-C* with liquid nitrogen by warming *T-B* with hot water. The sample tube is cut off with a hand torch. Subtracting the weight of sample tube from that of sample tube with H₂O, the percentage of water in the sample is determined.

Water is passed over uranium metal at 600–800°C to convert the water to hydrogen. The apparatus is so arranged that any unreacted water may be recycled and complete reaction assured. The percentage of water in the sample

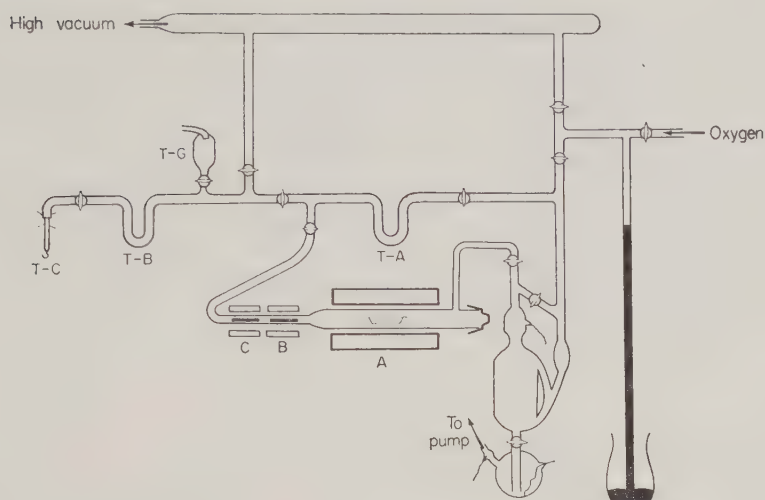


Fig. 1. The combustion apparatus.

can be determined again by measuring the pressure of the hydrogen in a known volume. The hydrogen is transferred to the sample tube by an automatic Toepler pump. The results are recorded relative to mean ocean water taken as $\delta D = 0$ and data quoted from the literature have been reduced to this standard.

The isotopic composition is measured with a 6" 60° mass spectrometer. The mass spectrometer used for this research was that of H. C. UREY's group (McKINNEY *et al.*, 1950). FRIEDMAN (1953) has described the details of the hydrogen mass spectrometer.

For the analysis of a water sample such as that of a liquid inclusion in a rock, and of other surface water, 10 mg of sample was used. The hydrogen sample was prepared by using the technique described above for the conversion of water to hydrogen. The overall error in analysis is usually less than ± 0.5 per cent.

The working standard gas was hydrogen of Lake Michigan water. Results are presented as differences, δD per cent, between the deuterium concentration in the sample and standard.

$$\delta D \text{ per cent} = \frac{D/H \text{ sample} - D/H \text{ standard}}{D/H \text{ standard}} \times 100$$

Considerable confusion in regard to standards exists. Lake Michigan water was used in the Chicago laboratories, and also an error of about 10 per cent occurred in some way in the enriched standard so that data reported from these laboratories showed a wider spread of data than the true values. We here refer all our data to the standard mean ocean water (SMOW) of EPSTEIN and MAYEDA (1953), which differs from the Bureau of Standards no. 1 by the relation:

$$(D/H)_{\text{SMOW}}/(D/H)_{\text{NBS-1}} = 1.05$$

and for O^{18} :

$$O^{18}/O^{16}_{\text{SMOW}}/O^{18}/O^{16}_{\text{NBS-1}} = 1.008$$

These values have been secured by CRAIG using the samples of EPSTEIN and

MAYEDA. We have calculated all data quoted from the literature to the same basis as nearly as we can estimate.

In terms of the SMOW standard, the Chicago Lake Michigan standard is -4.08 per cent, NBS-1 is -4.76 per cent and NBS-1^A is -18.33 per cent. These data define our data relative to standards available to other workers.

To check the effect of temperature at which water is extracted from silicates, perlite from Fish Springs and mica were heated at varying temperatures up to 1330°C for the perlite and to 1500°C for the mica. In mica the hydrogen is bonded as OH groups. KELLER and PICKETT (1954) reported the structure of perlite. It is shown diagrammatically in Fig. 2.

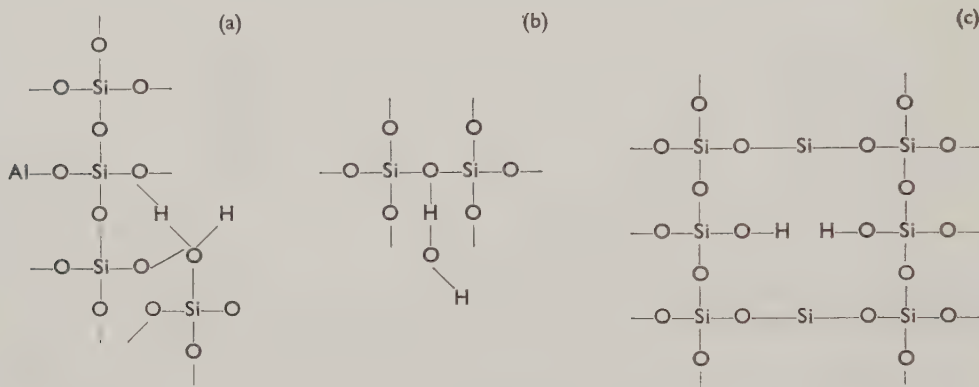


Fig. 2. Diagrammatic representation of the structure of perlite. After KELLER and PICKETT (1954).

Much of the water in perlite is hydrogen-bonded in the form shown in Fig. 2(a), and some as hydrogen-bonded water as in Fig. 2(b). Only part of the OH is monomeric as in Fig. 2(c).

The isotopic composition of each fraction of water given off different temperatures are given in Table 1.

It can be seen that a small amount of water is bound in the mica even at 1100°C and the lighter water is driven off at elevated temperature (1100 – 1500°C). However, to see the general tendency of isotopic composition, it may be enough to collect the water from 110 to 1100°C because the contribution of the fraction extracted above 1100°C is small compared with the main fraction between 110° and 1100°C . In this research we used the temperature range from 110 to 1100°C because of some difficulties in experimental apparatus.

The isotopic compositions of hydrogen in perlite and mica at different temperatures are interesting. Two kinds of behaviour of the isotopic composition are apparent from the water extraction processes in vacuum. The deuterium content of the different water fractions from perlite does not show any continuous increase or decrease with temperature until 800°C , whereas the heavier water is collected at elevated temperature (800 – 1100°C); the lighter water is collected at higher temperature (1100 – 1500°C) in the case of mica. The water collected between room temperature and 110°C is taken to be due to contamination.

Table 1. Water fraction extracted in vacuum at different temperatures from perlite and mica

(The samples were maintained at the indicated higher temperature for 1 hr after the temperature was attained.)

Sample	Temperatures (°C)	Water (%)	δD (%)
Perlite	Room temp.—110	0.38*	—3.6*
	110–180	0.19*	—16.0*
	180–300	0.93	—15.4
	300–410	1.00	—15.8
	410–800	0.59	—17.1
	800–1100	0.005	~ —9.3
	1100–1330	0.00	
	Total water (110–1100°C)	2.87	—16.0
	(Room temp.—1330)	3.24	—14.6*
Mica no. 1	110–1100°C	4.39	—5.9
	1100–1500°C	0.28	—11.7
	Total water (110–1500°C)	4.67*	—6.2*

* Values obtained from calculation. Observed data are:

Room temp. to 1100°C,	3.24% water,	δD —14.6%.
110°–1100°C,	2.87% water,	δD —16.0%.
180°–1100°C,	2.68% water,	δD —16.0%.

ANDERSON *et al.* (1937) noticed heavier water came off first when they dehydrated $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. VERNADSKY *et al.* (1941) found a fractionation when they expelled water from chlorites. The heavier water is expelled from the first fractions compared to that of the following higher temperature.

As far as our experiments are concerned, we observed two opposite results when we dehydrated minerals. The quantitative explanation of this different behaviour of water extraction at high temperature is not clear. We could not generalize the behaviour of the isotopic composition of water when we heated minerals in a vacuum.

The results for the analyses of the samples investigated in this research are given in Table 2.

The natural variations in the isotopic composition of terrestrial and meteoritic substances are summarized in Table 3 for the purpose of comparing them with the isotopic data of Table 2.

All waters from the minerals and rocks studied in this paper can be said to be from igneous rocks. It is, of course, necessary that the minerals and rocks which are now under consideration have not suffered any alteration or action of recycled water after their consolidation and that they have not been free to change their isotopic composition since.

The deuterium concentration of the liquid inclusions of the rocks from Japan is always less than that of ocean water but is about the same as that of surface waters of the same region. Also, the concentrations in the rocks and minerals from

Table 2. Hydrogen isotopic composition in minerals, rocks, and liquid inclusion from rocks*

Sample	δD (%)	H_2O (%)
Perlite	-16.0	2.87
Obsidian no. 2	-11.8	0.16
Marekanite	-11.3	0.29
Mica no. 1	-6.2	4.67
Mica no. 2	-5.9	4.39
Hawaii volcanic bomb	-8.5	0.09
Hawaii glassy spatter	-7.8	0.09
Mihara volcanic bomb	-6.2	0.07
Olivine basalt	-6.4	0.56
Huzi basalt no. 4	-9.4	0.21
Hatizyôzima basalt no. 1	-6.2	0.21
Kôzutô liparite no. 5	-2.5	2.17
		O^{18} (‰)
Liquid inclusion: A3	-4.3	
A4	-4.1	
Kuhara (pH 7.0)	-6.0	-8.5
Kuhara	-3.5	-4.3
Blb	-3.5	
B3a(1)	-3.3	
B3a(2)	-3.4	
B3b	-5.4	-7.1
Bl + Blb + B3	-4.2	-3.5
Imazu	-3.5	
Imazu (1/10)	-4.8	
Hukuoka river water	-4.7	-6.8
Hukuoka tap water	-4.4	-6.6
Hukuoka rain	-2.3	-3.9

*Sources and other information pertaining to these samples are listed in the Appendix.

the United States are markedly less than that of ocean water but it is difficult to be sure that this is not due to contamination by present or past surface waters. The volcanic bomb and glassy spatter from Hawaii have markedly less deuterium concentration than the oceans and the volcanic bomb and the basalts from Japan have lower concentrations as well. It is difficult to argue that these bombs and igneous rocks coming from the earth's interior are always contaminated in some way, and especially is this true of the Hawaiian samples for the reasons given in the introduction of this paper.

FRIEDMAN and SMITH (1958) found very similar results for fourteen obsidians with an average deuterium content of $\delta D = -11.4$. (Their results are recalculated relative to mean ocean water.) It is difficult to feel certain that they have measured juvenile water because their samples are mostly continental in origin or come from regions where the rainfall is very much lower in deuterium than ocean water.*

* These authors did not argue that the water was juvenile but they did maintain that it was of igneous origin.

Table 3. The isotopic composition of natural substances—SMOW = 0.0
D Enrichment (%) Lake Michigan water = -4.08%

Material	<i>D</i> (%)	References
Rain		
Kobe, Japan; Nov. 1953	-3.25	CRAIG (Private communication)
Honolulu; Mar. 26, 1953	-0.9	CRAIG (Private communication)
Oahu, Hawaii; Nov. 13, 1953	-0.5	CRAIG (Private communication)
Oahu, Hawaii; 5 rain gauges	+0.3	CRAIG (Private communication)
Manoa Valley; Dec. 1953	-0.3	CRAIG (Private communication)
Meteoric water	-31.8 ~ +4.2	FRIEDMAN (1953) CRAIG <i>et al.</i> (1956) CRAIG (Private communication)
Rivers and lakes	-15.3 ~ +1.1	BOATO (1954) and CRAIG (1957)
Hot spring waters	-15.3 ~ -1.3	BOATO (1954)
Hot spring waters (Japan)	-9.6 ~ +4.1	TITANI <i>et al.</i> (1957)
Ground waters (Japan)	-6.8 ~ +1.6	TITANI <i>et al.</i> (1957)
Surface waters	-15.3 ~ +0.7	FRIEDMAN (1953)
Hekla lava	-17.1	BOATO (1954)
Obsidians	-14.7 ~ -8.1	FRIEDMAN and SMITH (1958)
Iron meteorites	-11.3	EDWARDS (1955)
Carbonaceous meteorites		
7 samples	-15.3 ~ +4.2	BOATO (1954)
Average of 7 samples	-0.1	BOATO (1954)
Orgueil, France	+21.0	BOATO (1954)
Mokoia, New Zealand	+18.3	BOATO (1954)
Ivuna, Tanganyika	+26.9	BOATO (1954)
Murray, U.S.A.	+4.2	BOATO (1954)

It should be noted that these samples coming from the deep interior of the earth do not agree exactly in isotopic composition.

A correct estimate of the composition of average surface waters of the earth will not be identical with that of ocean water. The oceans contribute about 2.72×10^5 g/cm² of the earth's surface. Sediments contain about 4.1×10^4 g/cm² (HUTCHINSON, 1957). This fresh water contains about 10 per cent less deuterium than the oceans (FRIEDMAN, 1953). The ice of Antarctica and Greenland amounts to about 6×10^3 g/cm² and its deuterium concentration is about 75 per cent that of the oceans. The mean composition of all surface water is then 1.75 per cent less in deuterium than the ocean. It is evident that these juvenile waters do not agree with this estimate and we believe that the estimate of -1.75 per cent is a reasonable one.

We believe these differences in composition between juvenile sources and the surface waters to be real and offer the following possible interpretations of this conclusion.

(1) At some time in the past, there occurred a preferential escape of protium relative to deuterium from the earth. In the most favourable case, namely with no escape of deuterium, some 4 per cent of all the present oceanic hydrogen must

have escaped. This is equivalent to 1.25×10^4 g/cm² of oxygen or sixty times the amount of the present atmospheric oxygen. This oxygen is sufficient to account for the oxidation of the surface carbon from C to CO₂, of S²⁻ to SO₄²⁻, of NH₃ to N₂, and of all ferric iron of the crust from ferrous iron (UREY, 1953). This is a very large amount of oxidation and more than is usually assumed to have occurred.

(2) The surface water of the earth has not come entirely from the earth's interior, but some was present at the beginning and at that time had acquired an increased concentration of deuterium by some process during the earth's formation. It is interesting to note that the only sources of hydrogen having considerably increased concentrations of deuterium are several of the carbonaceous chondrites as shown in Table 3. No terrestrial sources of water or other hydrogen compounds having such greatly increased concentrations of deuterium are known and hence contamination cannot be the explanation of these data. Other carbonaceous chondrites have lower deuterium concentrations similar to that of the oceans and these concentrations are very variable, and this same variation occurs between adjacent samples of the same meteorite. Also, the isotopic composition of the carbon varies in a similar way. As BOATO concludes, such variation especially in the case of carbon can hardly have been produced by exchange after their arrival on earth.* This evidence and that presented in this paper and by FRIEDMAN and SMITH (1958) indicate that the meteorites and the earth may both have accumulated from samples of matter having variable abundances of deuterium. The extent of the variation could lie well within the limits expected for the chemical fractionation of the isotopes of hydrogen and carbon. In this case, the surface of the earth acquired water having a high deuterium content and this water has been diluted by water from the earth's interior by an unknown amount. Possibly studies of the isotopic composition of fossil hydrogen could demonstrate a decreasing or constant deuterium content with time and thus enable a decision between the two possibilities indicated in the present discussion.

Other samples of water investigated and reported in the tables do not contribute to the problem of the origin of the oceans and are reported here without comment as part of the general literature on the subject.

APPENDIX

Sample Descriptions

Perlite, from Fish Springs, about 7 miles south of Big Pine, Inyo Co., Calif., Pleistocene dome of vesicular perlite. Collected by Dr. R. MARSHALL.

Obsidian no. 2, from Glass Mountain, Aiskiyou Co., Calif. Collected by Dr. R. MARSHALL.

Marekanite, from Hondo Canyon, 3 miles north-west of Bear Springs, Jemez Puadrangle, Sandoval Co., New Mexico. Collected by Mr. R. L. SMITH.

Mica no. 1, muscovite mica separated from pegmatitic patches in granite,

* Fractionation by the loss of hydrogen and carbon while the meteorite was in space does not appear to be probable. Very considerable loss would be required unless the fractionation was very complete and this is especially improbable in the case of carbon. The carbonaceous chondrites do not appear to be the residue after a considerable loss of water and carbonaceous compounds.

Iron Co., Missouri. The sample is from a quarry and should be quite fresh. Collected by Prof. M. N. BASS.

Mica no. 2, muscovite mica from an exposed pegmatite knob, Camden Co., Missouri. The feldspar of the pegmatite is largely altered to kaolinite or other clays. Collected by Prof. M. N. BASS.

Hawaii volcanic bomb, collected from 1955 eruption (Kilauea, Hawaii) by Dr. G. A. MACDONALD.

Hawaii glassy spatter, collected from 1954 eruption (Kilauea, Hawaii) by Dr. G. A. MACDONALD.

Mihara volcanic bomb, collected from 1951 eruption (Mihara-yama, Tokyo, Japan) by Prof. I. IWASAKI.

Olivine basalt, from Imazu, Hukuoka, Japan. Mother rock of liquid inclusion from Imazu (KOKUBU *et al.*, 1957).

Huzi basalt no. 4, from Huzi volcano, Japan. Collected by Prof. I. IWASAKI.

Hatizyôzima basalt no. 1, from Hatizyôzima, Seven Izu Islands, Japan. Collected by Prof. I. IWASAKI.

Kôzutô liparite no. 5, from Kôzutô, Japan. Collected by Prof. I. IWASAKI.

Liquid inclusion: A3, from Kusuku, Saga Pref., Japan. Collected 22 March, 1949 (IWASAKI *et al.*, 1956).

Liquid inclusion: A4, from same locality. Collected 23 March, 1949 (IWASAKI *et al.*, 1956).

Liquid inclusion; Kuhara (pH 7.0), from Kuhara, Saga Pref., Japan. Collected 29 October, 1949 (IWASAKI *et al.*, 1956).

Liquid inclusion; Kuhara, from same locality. Collected 29 October, 1949 (IWASAKI *et al.*, 1956).

Liquid inclusion; Blb, from Kusuku, Saga Pref., Japan. Collected 30 October, 1949 (IWASAKI *et al.*, 1956).

Liquid inclusion: B3a(1), from same locality. Collected 30 October, 1949 (IWASAKI *et al.*, 1956).

Liquid inclusion: B3a(2), from same locality. Collected 30 October, 1949 (IWASAKI *et al.*, 1956).

Liquid inclusion: B3b, from same locality. Collected 30 October, 1949 (IWASAKI *et al.*, 1956).

Liquid inclusion: B1 + B1b + B3, from same locality. Collected 30 October, 1949 (IWASAKI *et al.*, 1956).

Liquid inclusion: Imazu, from Imazu, Hukuoka, Japan. Collected 16 July, 1955 (KOKUBU *et al.*, 1957).

Liquid inclusion: Imazu (1/10), from same locality. Above original solution was diluted to 1:9 for chemical analysis (KOKUBU *et al.*, 1957).

Hukuoka river water, from Susenzi, Maebara-mati, Itosima-gun, Hukuoka Pref., Japan. Collected 23 March, 1958 by Mr. Y. IDE.

Hukuoka tap water, from the spout of tap water in the laboratory of Kyusyu University (no. 4 Building of Faculty of Science), Hukuoka, Japan. Collected 10 April, 1958 by Mr. Y. IDE.

Hukuoka rain, collected at Kyusyu University between no. 3 and no. 4 Faculty of Science Building, Hukuoka, Japan, on April, 1958 by Mr. Y. IDE.

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Nickel analyses of metallic meteorites by the electron-probe microanalyser

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Abstract—The electron-probe microanalyser was used to obtain Ni analyses of separate phases in nine metallic and one stony meteorite. Proper surface preparation and adequate calibration were found to be important. Kamacite composition was uniform throughout the phase. In swathing kamacite, however, Ni became appreciably lower near a schreibersite inclusion. Taenite exhibited a marked composition gradient which increased at the taenite-kamacite interface. The Ni content of fine plessite was intermediate. It also exhibited a Ni concentration gradient, which was continuous with that of adjacent taenite. These facts accord with cooling of the original meteorite body or bodies over a long period of time to a temperature of 300°C or lower. The time was short of that required to produce uniform composition taenite, or uniform composition kamacite near schreibersite inclusions.

CHEMICAL analyses of metallic meteorites reported in the literature provide values for the overall Ni and Fe content. Such data are often variable and in poor agreement, even for the same section of a specimen, caused largely by difficulties of uniform sampling. Errors result particularly from localized non-metallic inclusions and the intrusion of oxides along grain boundaries. HENDERSON and PERRY (1954) discussed the relation of meteorite density to nickel content and advised favouring analyses of samples having normal metallic density in order to avoid errors from low-density inclusions. Also unresolved, however, is the additional problem of sampling and analysing kamacite, taenite and plessite uncontaminated by adjoining phases or inclusions, and without dissolving the interface metal, as in chemical separation techniques. Acid attack of the taenite surface, for example, obscures knowledge of the nickel content at the immediate phase boundary, such information being useful in estimating final temperatures and pressures at which kamacite and taenite reached equilibrium (UHLIG, 1954, 1955). Microhardness measurements of taenite have established probable composition gradients at the phase boundary, but fail to distinguish whether Ni or other elements are the cause (UHLIG, 1954, 1955; DALTON, 1950, 1951). X-ray measurements of lattice parameter have been useful in estimating the Ni content of kamacite and taenite, but these measurements are not particularly sensitive to composition differences, and they provide values integrated over the entire volume of sample, missing any compositional gradients.

All these difficulties are overcome in large measure by the electron-probe microanalyser. This instrument makes possible the quantitative analysis for Ni, and also many other metallic elements, in an area as small as $1\ \mu$ in diameter. Composition is integrated to a depth not exceeding about $1\ \mu$, hence errors caused by inclusions just below the surface are minimized. Furthermore, the analyses are non-destructive, hence specific areas of specimens can be re-examined at will, and final results established with greater certainty.

EXPERIMENTAL PROCEDURE

The possibility of obtaining chemical analyses by X-ray emission goes back to MOSLEY (1913). An instrument capable of microanalyses using this principle has become practical only recently through advances in electron optics. The principle and design of the present-day electron-probe microanalyser have been described elsewhere (CASTAING, 1952; BAILEY, 1958). This technique was apparently first applied to meteorite analysis by MARINGER *et al.* (1959). In brief, a focused narrow beam of electrons impinges on the specimen in vacuum generating X-rays at the area of impact which are characteristic of elements in the specimen. The X-rays pass through a window, and are diffracted by a lithium fluoride crystal. Wavelengths and intensities are recorded using a proportional counter and suitable recorders. The wavelengths indicate the elements present, i.e. they provide a qualitative analysis, while the intensities correspond to the concentrations of these elements.

The diameter of electron beam in the presently used probe ranged from 1 to 5 μ . Small meteorite specimens within the vacuum chamber could be moved using two microscrews, one of which was driven slowly by a clock motor, allowing a continuous intensity reading across the specimen. A microscope was built into the apparatus allowing a view of the specimen during bombardment.

A simplified relation for X-ray intensity to concentration of emitting element, where neither absorption of X-rays nor fluorescence produced by the continuous spectrum or characteristic radiation are taken into account, is given by the approximation of WILLIAMS (COMPTON and ALLISON),

$$\frac{I_A}{I_A^\circ} = C_A$$

where C_A is the concentration of element A in the alloy, I_A is the intensity of primary emission of element A in the alloy, and I_A° is the intensity of primary emission of pure element A. However, the actual relation is more complex and is best resolved empirically using a calibration curve. Calibration was accomplished using fourteen Fe-Ni alloys, vacuum-melted in the laboratory from carbonyl nickel and electrolytic iron. They were cast in helium by drawing into Vycor tubes 7 mm in diameter, then homogenized at 1050°C in helium for 24 hr. The alloys were cut into small pieces and mounted in Bakelite in the form of a rectangle measuring 1.7 $\times$ 1.2 cm. The specimens were electrically grounded to the apparatus through a metallic specimen holder. Each of the alloys, ranging up to 58% Ni, was analysed chemically. The corresponding calibration curve is shown in Fig. 1. Calibration curves were determined in general both before and after analyses of each meteorite specimen. All measured intensities I_A of the alloy were normalized by dividing by the measured intensity I_A° of pure Ni obtained at the same time as for the meteorite specimen. It is estimated that the relative Ni analyses are correct to within about ± 5 per cent of the given values.

SPECIMEN PREPARATION

It was found that surface preparation was of utmost importance in obtaining reliable results. Any chemical treatment of the alloy surface resulted in abnormally

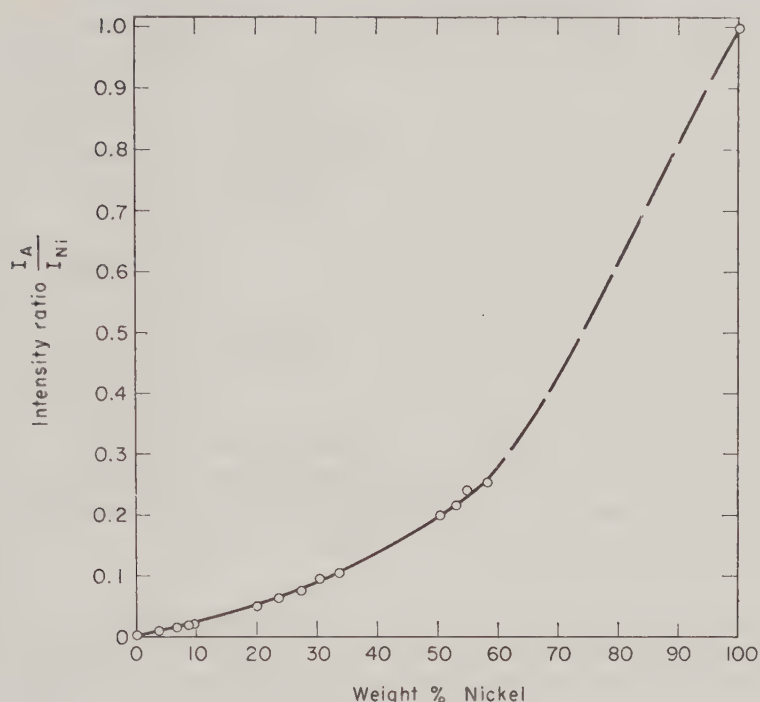


Fig. 1. Calibration curve.

high Ni results, brought about probably by superficial redeposition of metal from the electrolyte in contact through electrochemical action of local cells. For this reason all specimens, including the calibration alloys, were carefully polished using fine abrasives, omitting etching of any kind. Typical results showing abnormally high Ni values resulting from chemical etching or electropolishing are listed in Table 1. It was probably chemical etching which accounted for the extremely high Ni contents at the phase boundaries of Grant meteorite reported by MARINGER *et al.* (1959). Our results for the same meteorite are much lower. This factor is probably also the main reason for abnormally low Ni in kamacite and abnormally high Ni in taenite reported in the chemical analyses of several

Table 1. Effect of surface treatment on apparent nickel content of Fe-Ni alloys

Alloy	Mechanically polished	Electropolished*	Etched†
30.4% Ni (calibration alloy)	(30.4% Ni)	39.2% Ni	9.6% Ni 50.5%
Toluca, kamacite	7.6% Ni	39.2% Ni	
Toluca, taenite	36.1%	10.2% Ni	
(averaged for a band 0.04 mm wide)		52.0%	

* One-to-one part of acetic anhydride and HNO_3 .

† 1% HNO_3 in alcohol followed by 3% picric acid in alcohol.

meteorites by NICHIPORUK (1958). His technique of analysis and sampling required long periods of exposure of specimens to very dilute sulphuric acid during which time nickel ions in solution had ample time to redeposit on phases cathodic to kamacite, such as taenite and schreibersite, making analyses of taenite too high in Ni. Redeposition, on the other hand, diminished Ni concentration in the residual acid used as an index of kamacite composition, making the resulting Ni content too low.

The procedure adopted in this investigation was to first cut meteorite specimens slowly, using a band saw, to dimensions of about 0.8×0.6 cm. They were each mounted in Bakelite together with a small piece of pure Ni for calibration purposes as described above. Polishing was accomplished using four different grades of emery paper wet with water, followed by diamond paste of three different grades, the smallest particle size being $\frac{1}{4} \mu$. The specimens were mounted in the instrument in this condition and any etching was done after analysis was completed. A carbon trace, formed normally across the specimen surface by decomposition of residual oil vapours in the apparatus by the electron beam, served to mark the path of measured X-ray intensities.

RESULTS

Analyses for percentage nickel were obtained either from continuously recorded measurements across a specimen surface as shown for Grant meteorite (Fig. 2), with averaged results plotted with distance across the specimen in Fig. 3, or from point counts at various positions on the specimen surface. In either instance, an

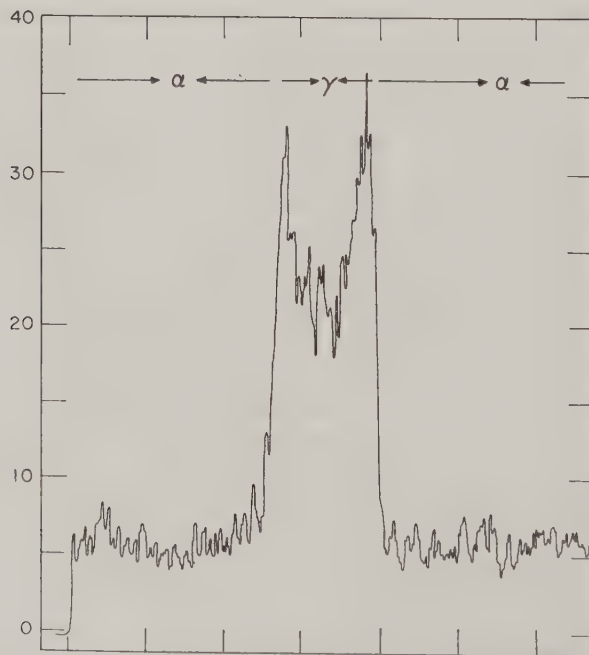


Fig. 2. Recorded intensity of Ni $K\alpha_1$ line across taenite phase of Grant meteorite (see Fig. 3).

arrow across the photomicrograph indicates the path and direction in which the analysis proceeded. Additional results for Grant are shown in Fig. 5, and for other meteorites in subsequent figures.

Local fluctuations in electron beam intensity obscured some of the fine details in curves for nickel analyses, but the averaged results for kamacite (α), taenite (γ) and plessite (α plus γ) were reasonably reproducible, as were the major compositional gradients in nickel content found in taenite at the α - γ -phase boundary. Small as was the electron beam diameter, its actual width tended to round out the discontinuity in nickel composition at the phase boundary, caused by unavoidable integration by the beam over a portion of both phases. Hence the actual slope probably changes more sharply from α to γ than is shown for example in Fig. 3. A beam of smaller diameter, as well as one with less "background" fluctuation, would provide a more accurate analysis of this important region.

However, some rounding of nickel composition at the phase boundary occurs even with a small diameter beam because of X-rays generated over a significant volume of alloy below the surface. Inclination of γ -phase to α -phase, as shown in Fig. 4, illustrates that as the beam progresses from α to γ at *A*, the beam generates

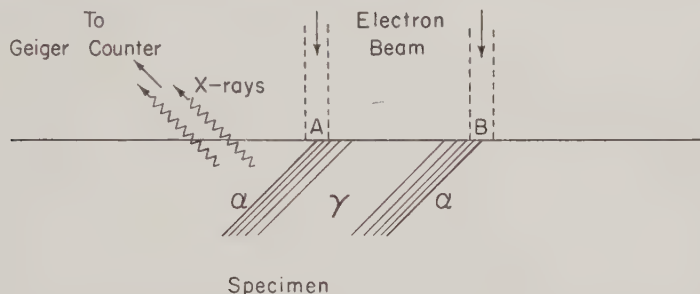


Fig. 4. Cross-section of taenite and kamacite illustrating schematically reasons for differing apparent Ni analyses at *B* than at *A*.

X-rays from increasing amounts of γ -phase before the beam reaches the actual phase boundary. The same thing happens at *B*, where increasing amounts of α -phase are included as part of γ -phase radiation before the beam reaches the phase boundary.

The above effect also accounts in part for lack of symmetry in Ni content across a taenite band, as is found in many meteorites but which is not expected to be real. Because of the nickel concentration gradient in γ -phase at *A* and *B*, the high nickel portion of γ at the phase boundary is diluted more by α -phase at *B* than at *A*, leading to lower apparent Ni at *B* than at *A*. This effect is dependent on the angle which γ -phase makes with the surface.

But probably the greater cause of asymmetry in Ni content is less dependent on the angle of γ -phase, and depends instead on absorption of X-rays* which are always recorded to one side of the specimen. X-rays generated by the beam at *A* are absorbed largely by α -phase, differing in degree from absorption occurring largely through γ -phase when the beam is at *B*. Although corrections for this and

* Pointed out to us by R. OGILVIE.

the above-described effect are possible, these have not as yet been adequately evaluated and the present results are reported without correction. A reasonable nickel content for taenite at the interface can be obtained presently by averaging the two reported peaks. This value, for reasons already discussed above, is somewhat below the actual expected maximum Ni content. How much higher nickel values reach, and how much, if any, gradient in nickel is found in kamacite at the immediate interface must await further analyses using, for example, a smaller diameter beam applying appropriate corrections for the actual beam diameter.

Grant is a medium octahedrite reported by HENDERSON (1941) to contain an overall nickel content of 9.35%. Analyses were carried out using nine different electron beam traces, typical of which are Figs. 3 and 5. These indicate that kamacite is constant in composition at 6.6% Ni, taenite varies from 23 to 32.4% Ni with highest Ni content at the γ - α interface, and plessite varies from 13 to 19% Ni with an average of perhaps 14.5% Ni. It was noted, e.g. Fig. 5, that plessite etches lighter or darker in certain areas suggesting at least two different kinds. Discontinuities in slope of Ni content across a plessite field in Grant and also in other meteorites confirm that compositional differences exist.

Canyon Diablo is a coarse octahedrite, chemical analyses for which vary from 7.1% to 7.3% (MERRILL, 1913; GOLDBERG *et al.*, 1951).^{*} Two specimens were purchased from the American Meteorite Museum, one having been found at the rim of Meteorite Crater, Arizona and the other several miles away from the rim. The specimen at the rim shows a granulated kamacite and vestigial Neumann bands, indicating, as pointed out by NININGER (1956), that the specimen was heated at elevated temperatures for a short but appreciable period. This is not characteristic of the other specimen found away from the rim which contains relatively clear kamacite and well-defined Neumann bands. One possibility is that heat treatment of the former specimen originated from its close proximity to the hot shattered rock blasted out to form the rim at the time of the meteorite impact, whereas specimens thrown clear of the rim were not subject to similar prolonged temperatures. A pertinent question is whether the two specimens were once essentially from the same original body. Chemical analyses as carried out at MIT by D. GUERNSEY indicated differing origin, drillings of the specimen at the rim showing an overall 7.52% Ni and for the specimen away from the rim 6.84% Ni.[†] Preliminary electron microprobe analyses obtained so far, support the viewpoint instead that the two specimens actually came from the same body. Data are summarized in Table 2 and Figs. 6 and 7.

Table 2. Electron-probe analyses of Canyon Diablo specimens

Phase	Specimen away from rim	Specimen at rim
Kamacite (α)	7.0% Ni	7.0% Ni
Max. Ni in taenite (γ)	31-34%	31%
Plessite ($\alpha + \gamma$)	20% min.	16.3% min.

^{*} A second smaller group of specimens found at Meteorite Crater called Canyon Diablo no. 2 analyse 8.1 to 8.2% Ni (GOLDBERG *et al.*, 1951) and 8.4% Ni (NININGER, 1940).

[†] Not excluding non-metallic inclusions.

Chemical analyses for kamacite of Canyon Diablo by FLORENCE quoted by FARRINGTON (1915, p. 132) provide values of 5.51 to 6.81% Ni which average somewhat lower than 7.0% Ni found presently. Taenite values, are quoted to range from 27.7 to 34.7% Ni (FARRINGTON, 1915, p. 134), falling to either side of the present maximum values.

A graphite nodule found at Meteorite Crater, Arizona, supplied by courtesy of NININGER, was also analysed both chemically and by the probe. The nodule measuring several inches in diameter contained several visible continuous narrow bands of metallic phase meandering throughout the specimen as if the graphite had been once a liquid and on solidification had rejected the metallic phase. Chemical analysis of the metallic phase by GUERNSEY of MIT showed 6.2% Ni, 0.4% Co, 77.9% Fe, 11.0% C and 4.5% unaccounted for. The electron-probe analysis showed 6.8% Ni. The latter value agrees reasonably well with the chemical value corrected for carbon content. It is interesting to note that some inclusions of what is presumably graphite within the metallic phase is in the form of regular hexagons as well as squares and equilateral triangles.

Glorieta Mountain is described as a stony-iron specimen (LOVERING *et al.*, 1957), the metallic phase of which, high in schreibersite, contains 11.79% Ni (HENDERSON, 1941). The metallic phase was analysed by two electron-beam traces. The nickel content was also determined for swathing kamacite around a schreibersite (phosphide) inclusion. Kamacite averaged 7.5% Ni, taenite varied from 26 to 32.5% at the kamacite boundary, reaching a minimum of 23.5% at the inner part of a narrow band (trace 2, Fig. 8), while plessite at the edge of the field reached a minimum of 15% Ni at the centre of the trace (trace 1, Fig. 8). Note that the kamacite inclusion (trace 1) has the same Ni content as the main body of kamacite.

As in Canyon Diablo, a kamacite containing as much as from 7 to 7.5% Ni seems high compared with analyses of various kamacites listed by FARRINGTON (1915, p. 132). PERRY (1944, p. 11) stated that kamacite contains a maximum of 6% Ni and that reported analyses as high as 7% were probably from samples contaminated by taenite. The present results suggest that the higher values may not have been in error. This matter requires further study, in particular the verification that electron-probe analyses provide results that are not too high, and that the early chemical techniques provide results that are not too low.

Swathing kamacite (Fig. 9) analyses 7.5% Ni at the outer boundary, but beginning at 0.4 mm along the indicated trace, or about 0.3 mm away from the outer boundary, the Ni content falls. Decrease of Ni content becomes especially pronounced about 0.4 mm from the inclusion along the trace, or at about 0.1 mm normal to the inclusion (black area of photomicrograph) reaching about 3.5% Ni at the inclusion itself. The two jogs found in the composition curve were reproducible and could have been the result of changes in diffusion rate brought about by changes in temperature or pressure during the original cooling of the meteorite body. These results confirm analyses of HENDERSON and PERRY (1958) showing that in Tombigbee the Ni content of swathing kamacite is lower than in the main body of kamacite.

Analyses for Dexter, a medium octahedrite of overall 7.9% Ni (UHLIG, 1954, 1955) show that transformed or acicular kamacite has a Ni content of 6.8%.

comparable with the Ni content of clear kamacite in other meteorites. Taenite reaches 32.3% at the kamacite-taenite boundary, and plessite contains a minimum of 14.5% Ni (Figs. 10 and 11).

El Capitan is a medium octahedrite reported to contain 8.4% Ni (HOWELL, 1895). Like Dexter it also contains acicular kamacite, which analyses 7.0% Ni. Maximum Ni content of taenite at the kamacite interface is 30%, decreasing to 20% Ni at the centre of a narrow band, and to 16.5% Ni at the centre of a broader band (Fig. 12). Plessite varies from a minimum of 11.5 to 16.0% Ni (Fig. 13).

Casas Grandes is a medium octahedrite analyzing 7.73% (COHEN, 1892) to 8.20% (incl. Co) Ni (PERRY, 1944, p. 127). It contains many small phosphide inclusions (rhabdites). Kamacite analyses 6% Ni. Taenite attains a maximum of about 30% Ni at the kamacite interface, with minimum of 24% Ni in the interior of a narrow band. Fine plessite in one determination analysed 11.5% Ni minimum, showing a steep concentration gradient at the taenite border (Figs. 14 and 15).

Xiquipilco (Toluca) is a medium octahedrite reported to contain 7.54 (COHEN, 1892), 8.25 (NICHIPORUK, 1958) and 8.31% Ni (GOLDBERG *et al.*, 1951). Five traces (one of which is shown in Fig. 16) indicate that the Ni content of taenite at the kamacite interface ranges from 30 to 42%, and at the interior of taenite the Ni content is from 20 to 32% Ni. Kamacite analyses 7.5% Ni and fine plessite reaches a minimum Ni content of 15% (Fig. 17). Taenite etching darker at the edges was noted in several other meteorites, the reason for which is not known. The Ni content appears to be higher in the darker regions, but this in itself is not a likely cause of the etching pattern because nickel confers corrosion resistance and should lead to lighter not darker etched surfaces. A more likely cause is a fine dispersion of phosphides or other impurities in the outer region of taenite near the kamacite interface.

Tombigbee River is a Ni-poor ataxite, the chemical analysis of which is reported to be 4.11% (FOOTE, 1899) to 4.39% Ni (HENDERSON and PERRY, 1958, p. 378). The average Ni content by electron-probe analysis was 3.3%, which for reasons unknown is appreciably lower. The probe analyses confirm that there is an appreciable negative gradient in nickel content toward non-metallic inclusions as was demonstrated by HENDERSON and PERRY (1958). At one such area, a decrease in Ni was noted to start at 0.25 mm from the inclusion, the composition reaching 2.5% Ni at the inclusion interface.

Dayton is a Ni-rich ataxite, the overall chemical analysis for which is 18.10% Ni (HENDERSON and PERRY, 1954). The average Ni content was 5.7% for kamacite and 33.1% for taenite (Fig. 18).

Preliminary analyses of the metallic inclusions, measuring from 0.05 to 0.1 mm across, of Plainview, Texas, a stony meteorite, were also carried out. The inclusions contain curved Neumann bands indicating that the particles were distorted after formation of the bands (Fig. 19) although perhaps by the same impact which produced the bands. Similar curved bands are observed in iron specimens hit by a bullet (UHLIG, 1954, 1955). Some particles show a transformation structure (Fig. 20). For purposes of analysis the specimen surface was coated with a thin (0.1 μ) aluminium film by evaporation in order to make the surface conductive. The calibration alloys were coated similarly. The Ni content of the metallic phase

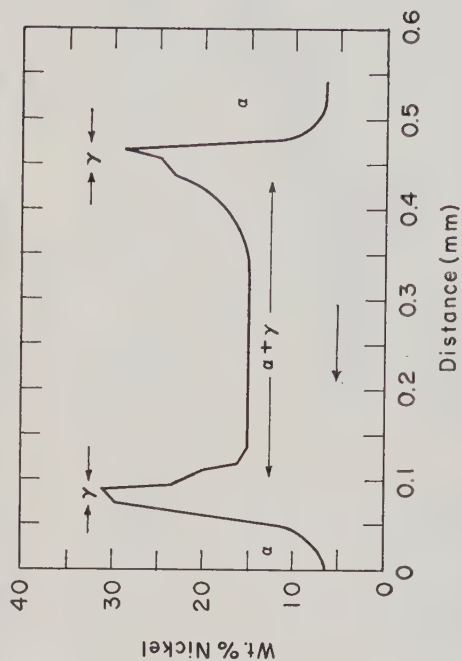


Fig. 5. Grant, $\times 60$. Analysis through kamacite (light back-ground), taenite (light border) and plessite (dark).

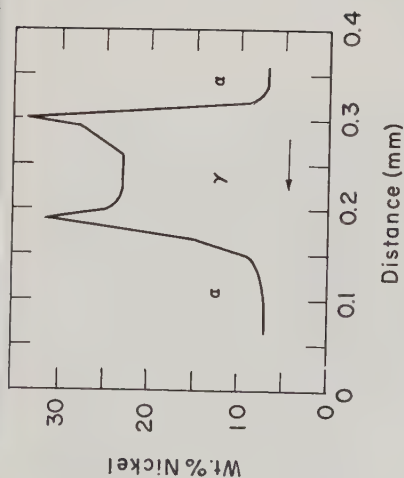


Fig. 3. Grant, $\times 60$. Variation of % nickel across kamacite (α) and taenite (γ). Arrow indicates path and direction of electron-probe trace.

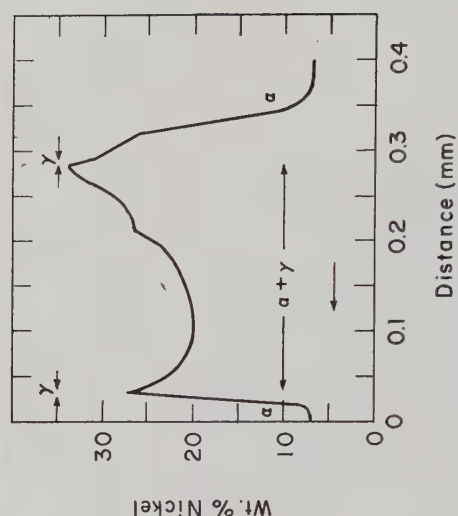
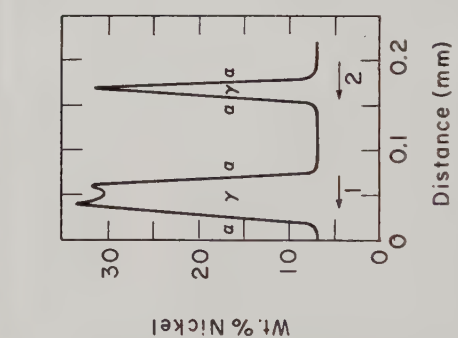


Fig. 6. Canyon Diablo at rim, $\times 60$. Analysis through taenite and fine plessite.

Fig. 7. Canyon Diablo away from rim, $\times 60$. Analyses through taenite band and plessite field.

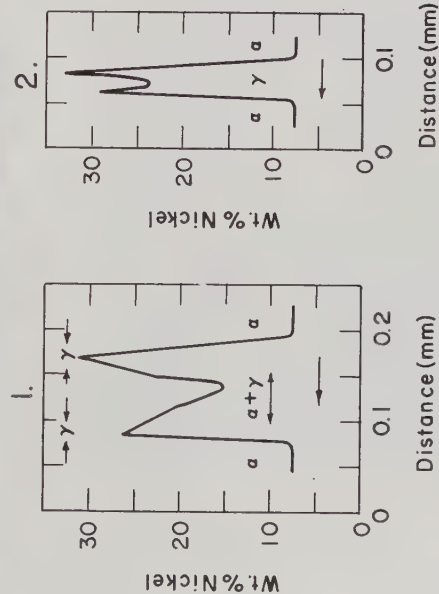


Fig. 8. Glorieta mountain. $\times 60$. Trace (2) crosses a taenite band; trace (1) crosses from kamacite to taenite, to plessite, to taenite, finally entering a kamacite inclusion.

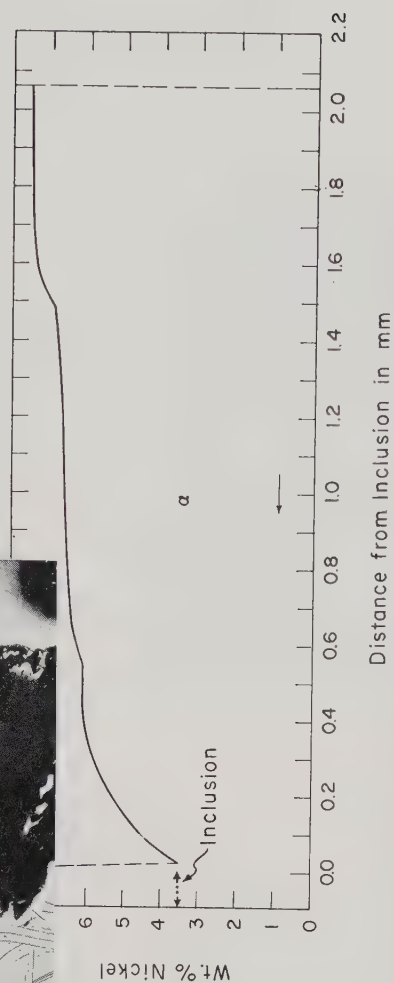
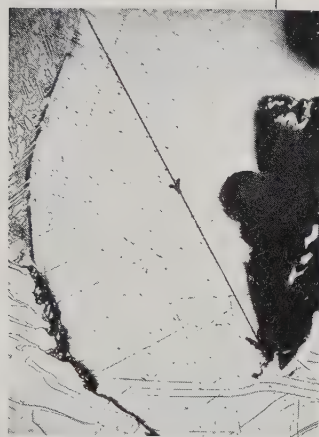


Fig. 9. Glorieta mountain. $\times 25$. Swathing kamacite around Schreibersite inclusion.

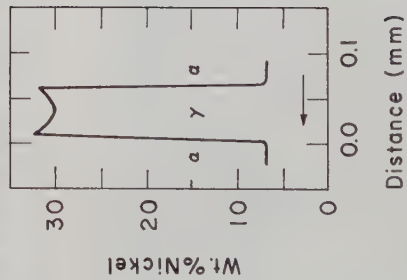


Fig. 10. Dexter. $\times 150$. Trace through taenite in acicular kamacite containing Neumann bands.

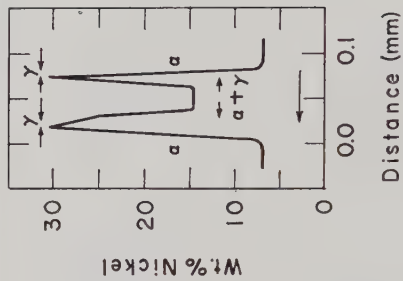


Fig. 11. Dexter. $\times 150$. Trace through fine plessite field.

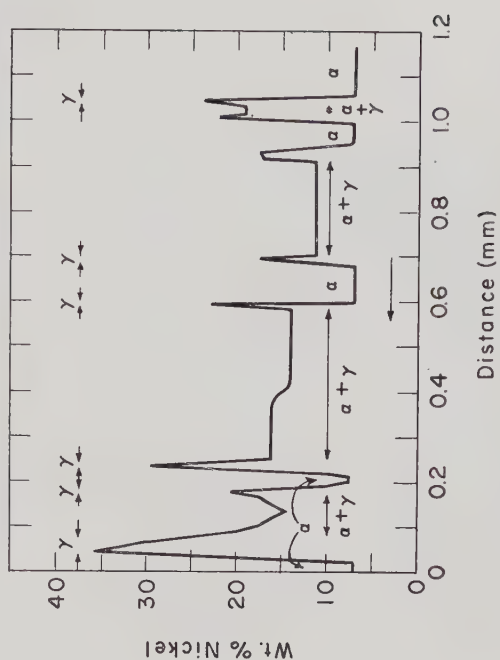


Fig. 13. El Capitan. $\times 60$. Trace through kamacite (acicular), taenite, plessite, kamacite, plessite, taenite, kamacite, taenite, plessite, taenite, kamacite, taenite, plessite, taenite, kamacite.

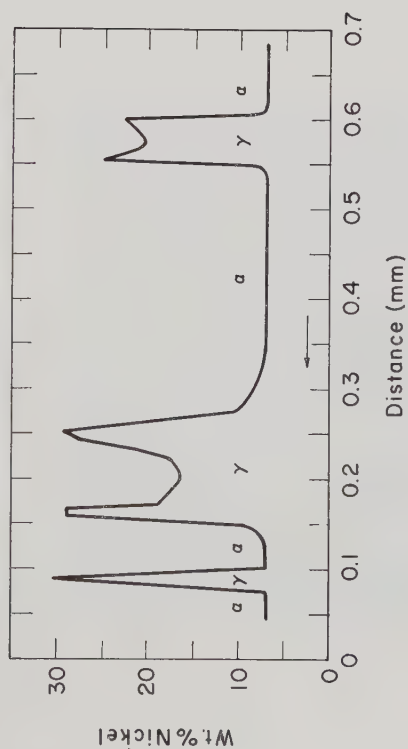
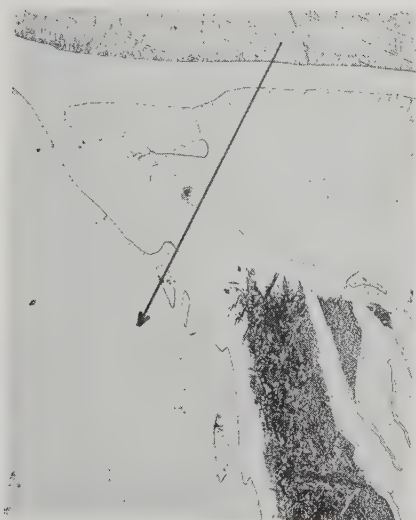


Fig. 12. El Capitan. $\times 60$. Trace through two taenite bands in kamacite.

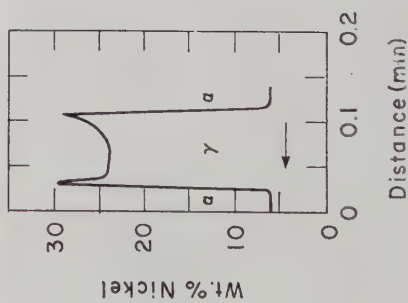
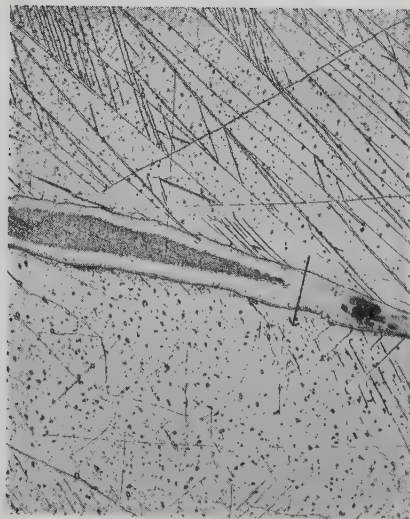


Fig. 14. Casas Grandes, $\times 60$. Analysis across narrow taenite band.

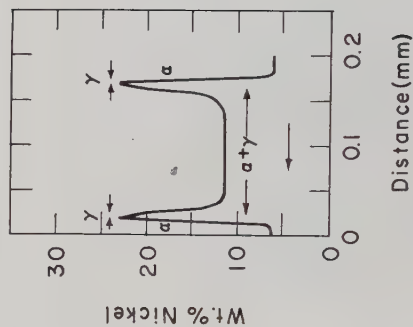
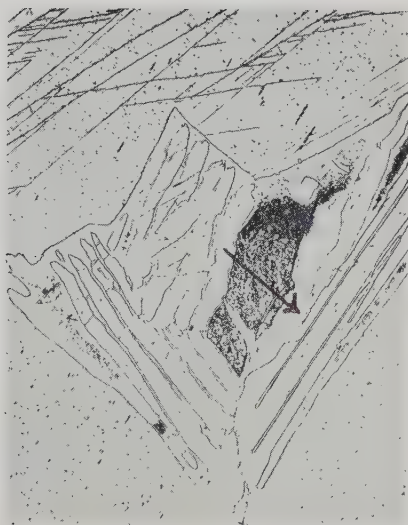


Fig. 15. Casas Grandes, $\times 60$. Analysis across plessite field.

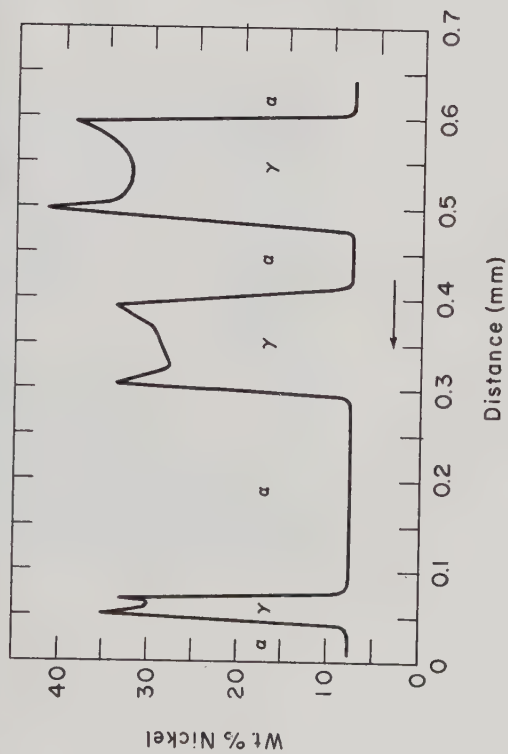
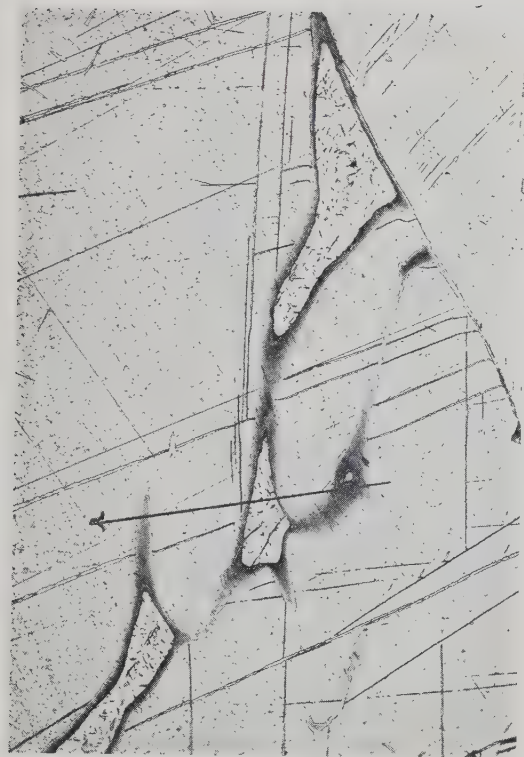


Fig. 16. Xiquipileo (Toluca). $\times 60$. Analysis across taenite bands.

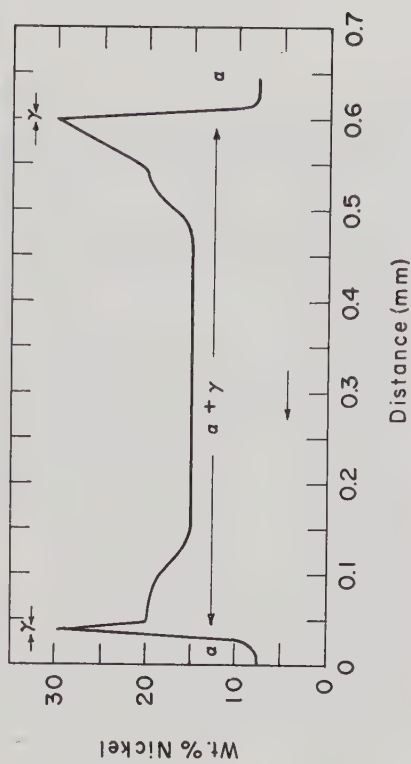


Fig. 17. Xiquipileo (Toluca). $\times 60$. Analysis across fine plessite field.



Fig. 18. Dayton. $\times 100$. Mixture of kamacite (light) and taenite (dark).

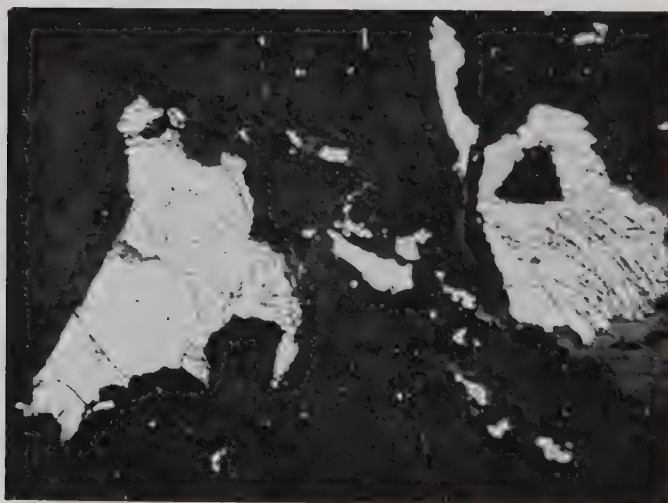


Fig. 19. Plainview (Texas). $\times 250$. Metallic inclusions of stony meteorite showing bent Neumann bands.

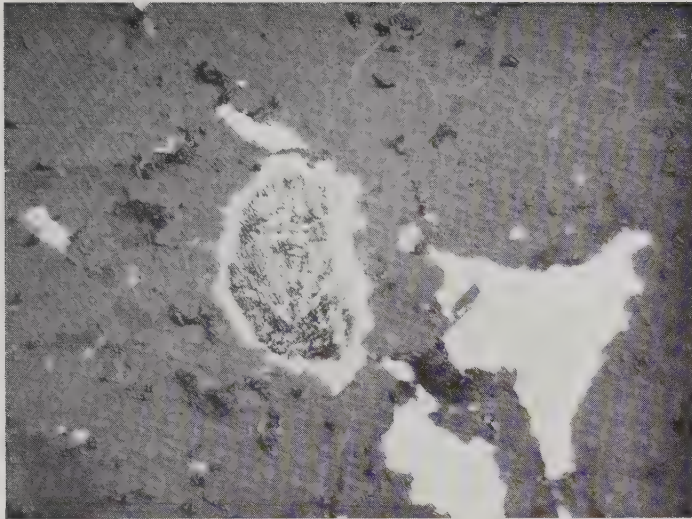


Fig. 20. Plainview, Texas. $\times 500$. Metallic inclusions one of which shows transformation structure.

was found to be 6.5% Ni without any observable gradient in Ni. These results support the conclusion that the observed transformation structure is acicular kamacite, similar to kamacite of Dexter and El Capitan.

Detailed interpretation of the foregoing results will be presented later. In general, the results are in line with the point of view, based on evidence presented earlier (UHLIG, 1954, 1955), that metallic meteorites cooled very slowly from the melt under high pressures. Continued cooling to low temperatures ($<300^{\circ}\text{C}$) under pressure accounts for an appreciable Ni concentration gradient in taenite and lack of a similar gradient in kamacite, the observed diffusion rate being much higher in the latter phase. Plessite is intermediate in Ni content, in line with the well-established evidence that it consists of a mixture of α - and γ -phases. Because present results establish that a Ni concentration gradient exists in fine plessite, the ratio of α - to γ -phases must change correspondingly. Also since the composition gradient is continuous with the observed Ni gradient in contiguous taenite, this fact lends support to the view (UHLIG, 1954, 1955) that plessite is a transformation product of taenite.

Acknowledgements—This research was supported by the National Science Foundation, to whom the writers express their appreciation. They are also grateful to R. OGILVIE and J. NORTON for making available the electron-probe microanalyser and for helpful discussions of the results. Finally, they appreciate the friendly cooperation of E. P. HENDERSON of the U.S. National Museum in supplying specimens of various meteorites.

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The Miller, Arkansas, chondrite

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Abstract—The Miller chondrite has been analysed, with the following results: Fe 19.90, Ni 1.60, Co 0.061, FeS 5.39, SiO₂ 38.13, TiO₂ 0.142, Al₂O₃ 2.06, Cr₂O₃ 0.32, FeO 4.74, MnO 0.31, MgO 23.71, CaO 1.61, Na₂O 0.82, K₂O 0.098, P₂O₅ 0.50, H₂O + 0.06, C 0.015. The mineralogical composition is orthopyroxene (En₈₂), olivine (Fo₈₂), plagioclase (An₁₀), nickel-iron, troilite, chromite, traces of diopside, and probably a little apatite; a single grain of native copper was seen on a polished surface of the meteorite. The density of the meteorite is 3.68.

INTRODUCTION

THE history of the Miller, Arkansas, chondrite is given by REEDS (1931). His description is repeated here in full.

“A New Meteorite.—The most recent accession by The American Museum of celestial immigrants is a stone meteorite from near Miller, Arkansas, which was acquired November 11, 1930, through the generosity of Mr. J. P. Morgan. It is a heart-shaped aerolite some twelve inches across by six inches thick, weighing 36 lbs. 10 oz. It was seen to fall at 9.00 a.m., Sunday, July 13, 1930, on the farm of Mr. Julian Bailey. One of the near-by witnesses likened the appearance of the flight of the meteor to that of a white pigeon, but moving much faster. The specimen raised a cloud of dust as it made a round hole 18 inches in depth in a dry dirt road-bed, fifty yards distant from the house of Mr. Bailey.

The entire surface of the specimen is coated with a thin black crust, a feature, which is characteristic of all stony meteorites. In a few places the crust has been scaled off, revealing a gray rock chondrite in texture. The specimen is unique in that the margins of the under surface are radially grooved. These markings, which were developed while passing rapidly through the earth's atmosphere, imply that the specimen did not turn over while in transit, but kept one face toward the earth.”

GENERAL DESCRIPTION

The external appearance of the stone is shown by photographs from two aspects (Figs. 1 and 2). The triangular form shown in Fig. 1 has the dimensions 32 cm × 32 cm × 30 cm, and the maximum thickness at right angles to this is 12 cm. The stone is completely covered with a skin of black glass up to 1 mm thick. In places this glass has flaked off, exposing the pale grey interior of the stone. The front surface of the stone is bluntly conical, and the glass shows flow lines radiating from the apex of the cone. The sides of the stone are notably furrowed, individual furrows being up to 3 mm deep; these furrows were evidently produced by the erosion of heated gases as the stone passed through the atmosphere. The glassy skin is notably thicker on the periphery of the underside of the stone, as it accumulated there after flowing back from the front surface and the sides.



Figs. 1 and 2. Photographs of top view (Fig. 1) and side view (Fig. 2). The dimensions of the stone as shown in Fig. 1 are 32 cm $\times$ 30 cm $\times$ 30 cm.

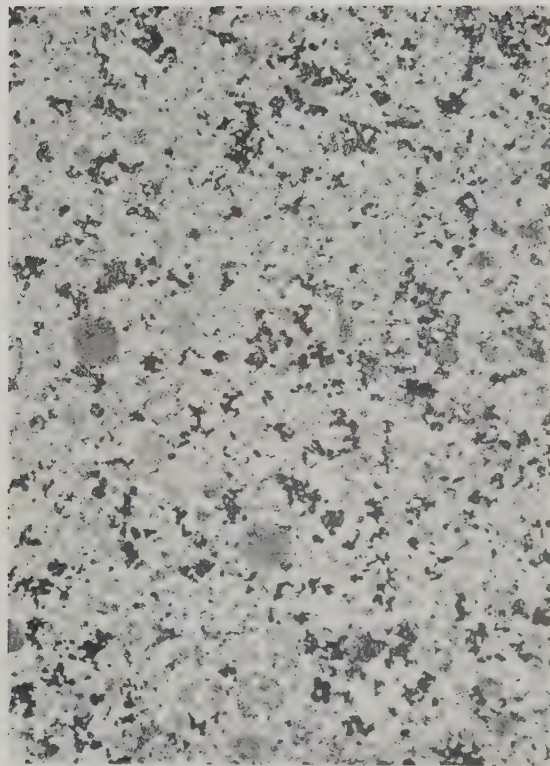


Fig. 3. Photomicrograph of a thin section of the Miller chondrite. Grey is bronzite, white olivine, black is nickel-iron, troilite, and chromite. Average diameter of chondrules 0.5 mm.

When crushed and examined under the microscope the glassy skin was found to be quite opaque, even in small fragments. A few grains of olivine were enclosed in the glass. An X-ray powder photograph of the glass shows only olivine lines, in contrast to a photograph of the interior of the meteorite, which shows strong lines of orthopyroxene as well as olivine. Evidently the temperature at the surface of the meteorite at the time the glass formed was sufficient to melt the orthopyroxene but not the olivine. From melting relations in the system MgO—FeO—SiO_2 (BOWEN and SCHAIRER, 1935) this indicates that the glass formed between about 1500 and 1600°C.

The interior of the stone is pale grey in colour, and a considerable amount of metal phase is visible to the naked eye. The stone is rather porous and friable. Broken surfaces are rapidly stained pale brown by a thin limonitic deposit, perhaps formed by the oxidation of a minute amount of lawrencite (FeCl_2) disseminated through the stone. When the stone is crushed many individual chondrules are found in the 10–60-mesh fraction.

The density of the meteorite was determined by placing a weighed piece in a beaker in a bell jar, evacuating with an oil pump to remove air from the pores, and then running in carbon tetrachloride and determining the apparent loss of weight on suspension in this liquid. The density thereby determined was 3.68.

MINERALOGICAL COMPOSITION

The minerals identified in the stone are orthopyroxene (bronzite), olivine, plagioclase, nickel-iron, troilite, chromite and diopside; a phosphate mineral (apatite or merrillite) is probably present in small amount. A single grain of native copper, 0.5 mm in diameter, was observed on the polished surface of this meteorite. Notes on the silicate minerals follow.

Bronzite. In view of the comparative lack of analyses of orthopyroxene from chondrites, we separated a pure fraction of this mineral from the Miller stone. About 40 g of the meteorite were crushed and treated with 1:1 HCl. This dissolved nickel-iron, troilite, and olivine. The washed and dried residue was centrifuged in methylene iodide ($D = 3.33$). The fraction which sank consisted of pure bronzite grains, grains of chromite, and bronzite grains with inclusions of chromite. On centrifuging this fraction in Clerici solution ($D = 3.43$) the chromite and the impure bronzite grains sank, and were thereby removed. The light fraction from this separation weighed 2 g, and was estimated to be at least 99 per cent bronzite. The bronzite was colourless and transparent, but with it were a few pale green grains. One or two of these were picked out and examined optically; they showed a somewhat higher birefringence than bronzite, had oblique extinction, and $\gamma = 1.702$, and are believed to be diopside. From the results of the above separation the density of the bronzite is estimated to be 3.38.

The analysis of this 2-g sample gave the results set out in Table 1. The analysis gave a figure of 1.56 per cent for Fe_2O_3 , which is probably entirely too high; in a meteorite with as much nickel-iron as Miller there should be little or no ferric iron, and the probable explanation is that this ferric iron is the result of oxidation of the bronzite during the separation procedures and subsequent analysis. We have therefore reported all iron as FeO. The CaO value is due in part only to the

presence of the small amount (less than 1%) of diopside mentioned above. A noteworthy feature is the presence of 1.22 per cent Al_2O_3 , which represents a considerable proportion of the total Al_2O_3 in the meteorite. Calculated mineral compositions of stony meteorites always allot Al_2O_3 to plagioclase, and this results in a uniformly too high percentage for this mineral. The TiO_2 content indicates that much of the TiO_2 shown in the bulk analysis of the meteorite is present in solid solution in the pyroxene.

Table 1. Analysis of bronzite from the Miller chondrite

	(1)	(2)		(3)	
SiO_2	55.51	0.9239	Si	1.971	2.000
TiO_2	0.21	0.0026	Al	0.029	
Al_2O_3	1.22	0.0119			
			Al	0.022	1.997
*FeO	11.46	0.1595	Ti	0.006	
MnO	0.55	0.0077	Fe	0.340	
MgO	30.08	0.7460	Mn	0.016	
CaO	0.58	0.0103	Mg	1.591	
$\text{H}_2\text{O} +$	0.0		Ca	0.022	
$\text{H}_2\text{O} -$	0.00				
	99.61				

* All Fe as FeO.

(1) Weight percentages.

(2) Molecular proportions.

(3) Atomic proportions calculated on the basis of six oxygen atoms.

The analysis agrees well with the accepted orthopyroxene formula $(\text{Mg},\text{Fe})\text{SiO}_3$. When the analysis is recalculated on the basis of three oxygen atoms the formula is $(\text{Mg}_{0.80}\text{Fe}_{0.17}\text{Al}_{0.01}\text{Ca}_{0.01}\text{Mn}_{0.01})(\text{Si}_{0.99}\text{Al}_{0.01})\text{O}_3$. Including Mn with Fe and Al and Ca with Mg the composition of this orthopyroxene is En_{82} , within the accepted composition limits of bronzite.

The refractive indices of the bronzite are: $\alpha = 1.669$, $\gamma = 1.681$. Using the γ -index as the most reliable, the composition according to some currently available curves relating refractive index to composition in the orthopyroxenes is as follows:

En_{87} (KENNEDY, 1947)

En_{90} (POLDERVAART, 1950)

En_{87} (HESS, 1952)

En_{84} (KUNO, 1954)

The curve of KUNO, which was based on orthopyroxenes from volcanic rocks, is in good agreement with the composition determined by chemical analysis, and is evidently the most satisfactory for use with meteoritic pyroxenes.

Olivine. The refractive indices of the olivine are: $\alpha = 1.670$, $\gamma = 1.706$, indicating a composition of Fo_{82} , according to the curve of POLDERVAART (1950). This has been confirmed by the X-ray method of YODER and SAHAMA (1957).

Plagioclase. The refractive indices of the plagioclase are $\alpha_1 = 1.536$, $\gamma_1 = 1.543$, indicating a composition of An_{15} .

Nickel-iron. An X-ray powder photograph of the metallic phase showed strong lines of kamacite and weak lines of taenite.

A thin section of this meteorite (Fig. 3) shows chondrules about 0.5 mm in diameter, of granular olivine and finely prismatic, sometimes radiating orthopyroxene, set in a granular ground mass of olivine, orthopyroxene, rare plagioclase and opaque material.

CHEMICAL COMPOSITION

The chemical analysis is given in Table 2, in the conventional form expressed as oxides, troilite and metal; in terms of the individual elements; and recalculated on a volatile-free basis.

Table 2. Chemical analysis of the Miller meteorite

(A)		(B)		(C)	
Fe	19.90	H	0.007	Na	0.93
Ni	1.60	C	0.015	Mg	22.17
Co	0.061	O	33.028	Al	1.68
FeS	5.39	Na	0.60	Si	27.64
SiO ₂	38.13	Mg	14.29	P	0.34
TiO ₂	0.142	Al	1.08	K	0.12
Al ₂ O ₃	2.06	Si	17.81	Ca	1.78
Cr ₂ O ₃	0.32	P	0.22	Ti	0.13
FeO	4.74	S	1.97	Cr	0.34
MnO	0.31	K	0.08	Mn	0.37
MgO	23.71	Ca	1.15	Fe	41.91
CaO	1.61	Ti	0.085	Co	0.09
Na ₂ O	0.82	Cr	0.22	Ni	2.48
K ₂ O	0.098	Mn	0.24		99.98
P ₂ O ₅	0.50	Fe	27.01		
H ₂ O +	0.06	Co	0.061		
C	0.015	Ni	1.60		
	99.46		99.46		

(A) Chemical analysis expressed as nickel-iron, troilite and oxides (all H as H₂O, all C as C (both free and combined)).

(B) Chemical analysis expressed as elements, with calculated figure for oxygen.

(C) Chemical analysis recalculated on a volatile-free (O, C, S, H) basis.

The normative mineral composition, expressed as weight percentages, is given in Table 3. This has been calculated as suggested by WAHL (1950), except that we prefer to calculate P₂O₅ as apatite, not merrillite; the composition of merrillite is not well established, being based on a single analysis of a small amount of impure material, and this mineral may well be a variety of apatite.

The normative mineral composition correlates well with the observed mineral

composition. The total amount of pyroxene is presumably a little greater than the sum of normative diopside and hypersthene (42.3 per cent), since a portion of the Al_2O_3 , calculated entirely as plagioclase, is present in the pyroxene. For the same reason the total amount of plagioclase will be somewhat less than the sum of normative orthoclase, albite and anorthite (9.2 per cent). The small amount of titanium is not present as ilmenite, but is in solid solution in the silicate phases.

Table 3. Normative mineral composition of the Miller meteorite

	(%)
Nickel-iron	21.56
Troilite	5.39
Olivine	18.87
Hypersthene	39.84
Diopside	2.44
Albite	6.91
Anorthite	1.64
Orthoclase	0.62
Apatite	1.18
Chromite	0.47
Ilmenite	0.26

An attempt to correlate the composition of the silicates, as given by the data on the bronzite and olivine, with the bulk composition of the meteorite, reveals a considerable discrepancy. Taking the composition for the bronzite given by chemical analysis, and that for olivine deduced from X-ray and optical data, the total percentage of MgO should be 21.6 (against 23.71 actually found) and FeO would be 8.3 (against 4.74 actually found). The percentage of FeO in the bulk analysis is probably too low. This value is namely a calculated figure representing the iron remaining after metallic iron and iron as FeS has been deducted from the total iron. Both the metallic iron (determined by the $\text{HgCl}_2\cdot\text{NH}_4\text{Cl}$ extraction method) and the FeS (obtained by calculating all S as FeS) tend to be too high and hence the FeO is too low. If oldhamite (CaS) and daubreelite (FeCr_2S_4) are present their S will be calculated as FeS, and thereby decrease the amount of iron calculated as FeO. A satisfactory method of determining FeO directly in the presence of sulphides and nickel-iron is not known.

The bulk chemical composition of Miller is close to that of Ochansk (WILK, 1956). However, the Al_2O_3 content of Ochansk (4.11 per cent) is twice as high as that of Miller (2.06 per cent). The Al_2O_3 in Ochansk is probably too high. It was obtained indirectly, as Al_2O_3 usually is in silicate analysis, whereas the Al_2O_3 content of Miller was determined by the direct method of WATTS (1958).

The chemical analysis shows that the Miller stone, in Prior's classification, falls into his group of bronzite-olivine chondrites. According to the classification of UREY and CRAIG (1953), it belongs to their H group, since it contains high total iron (27.01 per cent, the average for the H group being 28.58 per cent).

Acknowledgements—We are indebted to the J. Lawrence Smith Fund of the National Academy of Sciences for a grant towards the cost of this investigation. We would also like to express our

thanks to Dr. H. S. YODER, Jr., for assistance in the determination of the composition of olivine by his X-ray method, and to Mr. J. WEBER for the photomicrograph.

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The Kyushu, Japan, chondrite

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Abstract—The Kyushu chondrite has been analysed, with the following results: Fe 6.27, Ni 1.34, Co 0.046, FeS 5.89, SiO₂ 39.93, TiO₂ 0.14, Al₂O₃ 1.86, Cr₂O₃ 0.54, FeO 15.44, MnO 0.33, MgO 24.71, CaO 1.70, NaO 0.74, K₂O 0.13, P₂O₅ 0.31, H₂O + 0.27, C 0.03; total 99.67. The mineralogical composition is olivine (Fo₇₄), hypersthene (En₇₈), maskelynite, nickel-iron, troilite, chromite and possibly apatite. The density of the meteorite is 3.53.

INTRODUCTION

ON 26 October 1886, at about three o'clock in the afternoon, a shower of meteoritic stones fell over a considerable area of the southern part of the island of Kyushu, in the provinces of Satsuma and Osumi. The synonymy of this meteorite fall is extensive, since both province and village names have been applied to individual stones from this fall, and different transliterations have been used. PRIOR and HEY (1953) give the following names as synonyms: Ensighahara; Hanakai; Hishikari; Maeme; Oguchimura; Ogutimura; Oshima; Oynchimura; Satsuma; Shigetome; Sigetome; Simagoe; Yamanomura; Yenshigahara; possibly Kanzaki. Since PRIOR and HEY accept the name Kyushu this will be used here, although KANDA (1952), in his list of Japanese meteorites, records the fall under the name Satsuma.

The first reference to this fall we have found in the literature is a brief statement by CLARKE (1888), as follows: "The United States National Museum has recently received fragments of two new Japanese meteorites from the Educational Museum at Tokio. Both are greyish stones, showing a dull black crust. The first of the two fell at Fukutomi, Kinejima, Province of Hizen, March 19, 1882, at 1 p.m. Its total weight was 7680 grams. The second fell at Maeme, Hislugari, Province of Satsuma, November 10 (*sic*), 1886, at 3 p.m. Its original weight was 328 grams." The second fall is that now described as Kyushu.

The circumstances of the fall, and the surface features of some of the stones, were extensively described by JIMBO (1906). One of the stones was later figured and described in detail by HIKI (1912). KANDA (1952) states that the total weight of the fall was 46.41 kg. PRIOR and HEY (1953) record the following distribution of material from this fall: 4½ kg. in Tokyo Science Museum; 920 g in Tokyo University; 840 g in the Geological Institute of Tokyo; 9½ kg in The American Museum of Natural History, New York; 31.3 kg (including the largest stone, 28.8 kg) in the British Museum (Natural History), London. Smaller amounts are present in other meteorite collections.

As this meteorite seems never to have been analysed either mineralogically or chemically, we decided to do so, and selected from the collection of The American Museum of Natural History a single stone (catalog no. 1072, weight 815 g) for this purpose.

MINERALOGICAL COMPOSITION

The stone selected for investigation was completely coated with a thin black glassy crust. The interior was pale grey in colour, irregularly stained with thin films of brown limonitic material, probably produced by the oxidation of a small amount of lawrencite (FeCl_2). The density was determined on a piece weighing 170 g. This piece was placed in a beaker under a bell jar, and the jar evacuated by an oil pump to remove air from the pores; carbon tetrachloride was then run in, and the apparent loss of weight on suspension in this liquid measured. The density thereby determined was 3.53.

The minerals identified in the stone are: olivine, hypersthene, maskelynite, nickel-iron, troilite, and chromite; a phosphate mineral (apatite or merrillite) is probably present in small amount. Notes on the silicate minerals follow:

Olivine. The indices of refraction are: $\alpha = 1.683$, $\gamma = 1.721$, indicating a composition of Fo_{74} , according to the determinative curve of POLDERVAART (1950). This has been confirmed by the X-ray method of YODER and SAHAMA (1957).

Hypersthene. The indices of refraction are: $\alpha = 1.679$, $\gamma = 1.689$, indicating a composition of En_{78} , according to the determinative curve of KUNO (1954).

Maskelynite. This material, which is present in small amount, was separated by digesting a sample of the meteorite powder in 1:1 HCl (thereby dissolving nickel-iron, troilite and olivine), and obtaining a concentrate of maskelynite by centrifuging the residue in an acetone-methylene iodide mixture of density 2.9. The maskelynite was in the light fraction. It is isotropic or practically isotropic with an index of refraction of 1.502, corresponding to a plagioclase glass of composition An_{16} , according to the data of FOSTER (1955).

Dr. H. S. YODER, Jr., of the Geophysical Laboratory has examined the maskelynite and writes as follows: "The glass from the meteorite is exceptionally interesting. I have circled a spot on the thin section where I see blades of feldspar in glass. They appear to have grown in the glass. Some of the low index crystals in the glass of the powdered sample have all the aspects of the quench products often observed in studies of synthetic melts. On the other hand we see large feldspar crystals of irregular outline in glass in the separated powder. These I presume were partially melted." Dr. YODER's observations thus suggest that the maskelynite has been formed by the melting of pre-existing plagioclase, followed by rapid quenching of melt.

An X-ray powder photograph of nickel-iron separated magnetically from the crushed meteorite shows strong lines of kamacite and weak lines of taenite.

A thin section of the meteorite shows chondrules 0.5–1 mm in diameter, of both olivine and hypersthene, set in a granular groundmass of olivine, hypersthene and opaque material (nickel-iron, troilite and chromite). The maskelynite occurs as interstitial material, clear, isotropic, and with low relief. A certain amount of brown limonitic staining is associated with the opaque material.

CHEMICAL COMPOSITION

The chemical analysis is given in Table 1, in the conventional form expressed as oxides, troilite and metal; in terms of the individual elements; and recalculated on a volatile-free basis.

The normative mineral composition, expressed as weight percentages, is given in Table 2. This has been calculated as suggested by WAHL (1950), except that we prefer to calculate P_2O_5 as apatite, not merrillite; the composition of merrillite is not well established, being based on a single analysis of a small amount of impure material, and this mineral may well be a variety of apatite.

Table 1. Chemical analysis of the Kyushu meteorite

(A)		(B)		(C)	
Fe	6.27	H	0.029	Na	0.89
Ni	1.34	C	0.03	Mg	24.55
Co	0.046	O	36.82	Al	1.61
FeS	5.89	Na	0.54	Si	30.75
SiO ₂	39.93	Mg	14.90	P	0.23
TiO ₂	0.140	Al	0.98	K	0.16
Al ₂ O ₃	1.86	Si	18.66	Ca	1.99
Cr ₂ O ₃	0.54	P	0.14	Ti	0.13
FeO	15.44	S	2.15	Cr	0.61
MnO	0.33	K	0.10	Mn	0.43
MgO	24.71	Ca	1.21	Fe	36.30
CaO	1.70	Ti	0.08	Co	0.076
Na ₂ O	0.74	Cr	0.37	Ni	2.21
K ₂ O	0.13	Mn	0.26		
P ₂ O ₅	0.31	Fe	22.02		99.94
H ₂ O +	0.27	Co	0.046		
C	0.03	Ni	1.34		
	99.67		99.67		

(A) Chemical analysis expressed as nickel-iron, troilite and oxides (all H as H₂O), all C as C (both free and combined).

(B) Chemical analysis expressed as elements, with calculated figure for oxygen.

(C) Chemical analysis recalculated on a volatile-free (O, C, S, H) basis.

Table 2. Normative mineral composition of the Kyushu meteorite

	%
Nickel-iron	7.66
Troilite	5.89
Olivine	42.60
Hypersthene	28.93
Diopside	4.10
Albite	6.21
Anorthite	1.36
Orthoclase	0.78
Chromite	0.78
Apatite	0.74
Ilmenite	0.26

The normative composition correlates well with the observed mineral composition. No diopside was observed, and the calcium is probably present in solid solution in the hypersthene. The normative pyroxene is 33.03 per cent, normative olivine 42.60 per cent, giving a ratio of pyroxene to olivine of 3:4, which agrees

with estimates from thin sections and X-ray powder photographs. Normative feldspar is 8.35 per cent, which is probably higher than the amount of maskelynite present, since some of the Al_2O_3 calculated as feldspar is in the pyroxene. The 0.78 per cent normative chromite corresponds to the amount seen on polished surfaces. Although neither apatite nor merrillite were observed in thin section, the 0.74 per cent apatite in the norm could well be present; it would be extremely difficult to recognize it in a thin section, since it probably occurs in small grains intimately mixed with pyroxene and olivine. The small amount of titanium calculated as ilmenite is almost certainly in solid solution in the olivine and pyroxene.

A cross-check between the chemical analysis and the mineralogical composition can be obtained by calculating the amount of FeO and MgO required for the observed composition of the olivine and pyroxene, and comparing these figures with those given by the analysis. These results are as follows: FeO (analysis) 15.44 per cent (calculated) 14.7 per cent; MgO (analysis) 24.71 per cent, (calculated) 25.1 per cent. In view of the uncertainties in the derivation of the chemical composition of the minerals from their optical properties, and the difficulty of arriving at a precise figure for FeO by chemical analysis, the agreement is good.

The chemical analysis shows that the Kyushu stone, in Prior's classification, falls into his group of hypersthene-olivine chondrites of the Baroti and Soko-Banja types. According to the classification of UREY and CRAIG (1953), it belongs to their L group since it contains low total iron (22.02 per cent, the average for their L group being 22.33 per cent). Kyushu is closely comparable chemically and mineralogically with Holbrook (MASON and WILK, 1960) and a number of other hypersthene-olivine chondrites.

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The Holbrook, Arizona, chondrite

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Abstract—The Holbrook chondrite has been reanalysed, with the following results: Fe 7.18, Ni 1.09, Co 0.054, Cu 0.0096, FeS 7.94, SiO₂ 40.11, TiO₂ 0.14, Al₂O₃ 1.90, Cr₂O₃ 0.51, FeO 12.01, MnO 0.37, MgO 25.18, CaO 1.74, Na₂O 0.93, K₂O 0.10, P₂O₅ 0.40, H₂O 0.27, C 0.06; total 99.99. The mineralogical composition is olivine (Fo₇₄), hypersthene (En₇₆), plagioclase (An₁₅), nickel-iron, troilite, chromite, and possibly apatite. The density of the meteorite is 3.56. A summary of the data on the abundances of Ba, Bi, Cs, Cu, In, Pb, Li, Hg, Rb, Sc, Se, Sr, Te, Tl, Th, U, V, Y and Zr in this meteorite is included.

INTRODUCTION

ON 19 July, 1912, a shower of stony meteorites fell near the section house of Aztec, on the Santa Fe Railway some 6 miles east of Holbrook, Navajo County, Arizona. The circumstances of the fall were described by FOOTE (1912) and MERRILL (1912). FOOTE states that the fall occurred between 6.20 and 6.40 p.m., whereas MERRILL quotes the *Holbrook News* as saying that the fall took place about 7.15 p.m. The location of the fall, according to FOOTE, is 34°57' N, 110°2' W, but PRIOR and HEY (1953) give it as 34°54' N, 110°11' W; the latter figures are for the town of Holbrook, not for the actual place of fall, for which those of FOOTE are correct. The stones were scattered over an elliptical area roughly estimated by two finders to be about 3 miles long and $\frac{1}{2}$ mile wide. FOOTE, at that time operating the Foote Mineral Company of Philadelphia, arranged to purchase all stones collected, and over a period of 2 months obtained more than 14,000 stones (twenty-nine ranged in size from 1020 to 6665 g, 6000 from 1 to 1000 g each, and the remainder were smaller). He recovered a total weight of 208 kg, and he estimated that some 10 kg was kept by the finders or otherwise distributed; the total weight of the fall was thus at least 218 kg. Specimens of the Holbrook fall have been widely distributed, and it is intriguing to note that the comprehensive catalogue of PRIOR and HEY (1953) lists the whereabouts of some 87 kg, leaving a large amount unaccounted for. Much of this material is presumably in institutional and private collections throughout the world.

The mineralogical and chemical composition of the Holbrook meteorite was described both by FOOTE (1912) and MERRILL (1912), the comprehensive chemical analysis in MERRILL's paper being the work of J. E. WHITFIELD. However, as WAHL (1950a) pointed out, this analysis is unreliable, showing only a trace of Na₂O. As the Holbrook chondrite is excellent research material, being fresh and unaltered, is available in many institutions, and has been used in a number of investigations of minor and trace elements in meteoritic material, we decided to reanalyse this meteorite. We selected a single stone (catalogue no. 586) from the collection of The

American Museum of Natural History, weighing 2316 g, for investigation. We have also made some chemical determinations on material from the Chicago Natural History Museum.

GENERAL DESCRIPTION

The circumstances of the fall, and the surface features of the stones, have been well described by FOOTE. The individual stones, even the smallest, are usually completely covered with a thin crust of black glassy material. The glassy crust on some of the stones, especially the larger ones, shows typical radial flowage lines and thereby indicates the front end of the stones as they passed through the earth's atmosphere. The interior of the stones is compact, and light grey in colour, and the broken surface shows small particles of nickel-iron and larger particles of troilite; the silicates are very fine-grained, but occasional chondrules are visible to the naked eye.

The density of a weighed piece of the analysed specimen was determined by evacuating (by means of an oil pump) the piece under a bell jar, and then running in carbon tetrachloride and measuring the apparent loss of weight. By this technique it was hoped to avoid error caused by retention of air in the slightly porous meteorite. The density thereby determined was 3.56. This is probably more nearly correct than the figure 3.48 given by MERRILL.

The potassium-argon age of the Holbrook meteorite was determined by GEISS and HESS (1958) and found to be $4.4 \pm 0.1 \times 10^9$ years.

MINERALOGICAL COMPOSITION

The minerals identified in the stone are olivine, hypersthene, plagioclase, troilite, nickel-iron, and chromite; apatite (or merrillite) is probably present in small amount but was not identified. Merrill records occasional monoclinic pyroxene; however, we have carefully examined a pyroxene concentrate from this meteorite and have found only orthorhombic pyroxene. TOMLINSON, who described the mineralogical composition in FOOTE (1912), claims the presence of magnetite as small black grains in the mass of the meteorite; we believe, however, that this mineral was actually chromite (although there is probably a little magnetite in the glassy crust). TOMLINSON also described the occurrence of a patch of red-brown spinels set in quartz; MERRILL saw nothing of this sort, and nor have we. From TOMLINSON's description the quartz may have been plagioclase and the red-brown spinels chromite, which would accord with the overall composition of the stone; the occurrence of free quartz in a stone with so much olivine is improbable. Optical data on the individual minerals are as follows.

Olivine. The indices of refraction are: $\alpha = 1.683$, $\gamma = 1.722$; these indices indicate a composition of Fo_{74} , according to the data of POLDERVAART (1950); this composition was confirmed by the X-ray method of YODER and SAHAMA (1957).

Hypersthene. The indices of refraction are: $\alpha = 1.677$, $\gamma = 1.691$; these indices indicate a composition of En_{76} , according to the determinative curve of KUNO (1954).

Plagioclase. The indices of refraction are: $\alpha_1 = 1.535$, $\gamma_1 = 1.543$; these indices indicate a composition of An_{15} .

By treating a sample of the crushed meteorite with 1:1 HCl olivine, nickel-iron,

troilite, and probably apatite were dissolved, leaving a residue of hypersthene, plagioclase and chromite. The silica produced by the decomposition of the olivine was removed by dissolving in Na_2CO_3 solution. In this way pure grains of hypersthene and plagioclase were isolated for determinations of refractive index.

The nickel-iron in the Holbrook meteorite has been carefully studied by UREY and MAYEDA (1959), who recognized kamacite, taenite and plessite. An X-ray powder photograph of the nickel-iron showed strong lines of taenite and weak lines of kamacite.

The troilite was separated and analysed by WHITFIELD (MERRILL, 1912), who obtained Fe 63.62, S 36.50, Ni, Co, Cu, none; a result close to the theoretical composition of FeS .

Diamonds have been searched for in the Holbrook meteorite (UREY *et al.*, 1957); they found none, and give <0.02 per cent as an upper limit for the possible diamond content.

A thin section of the meteorite shows chondrules, 0.5–1.5 mm in diameter, of granular olivine and finely prismatic, sometimes radiating hypersthene, set in a fine-grained (0.1 mm diameter and smaller) ground-mass of olivine and hypersthene. Irregular opaque grains of nickel-iron, troilite and chromite are present, varying in size from 1 mm across down to dust-like material dispersed through the ground mass. A very small amount of brown limonitic staining is associated with some of the opaque grains. No plagioclase was identified in thin section, although it was found in the residue left after dissolving a portion of the meteorite in 1:1 HCl; it is present in small amount evidently as very small interstitial grains.

It should be noted that both the hypersthene and olivine give sharp peaks in the X-ray diffractometer, implying that the composition of both these minerals is quite uniform. This is supported by the optical data. The association of an olivine with hypersthene with a somewhat higher $\text{Mg}/\text{Fe} + \text{Mg}$ ratio is consistent with equilibrium crystallization in the system $\text{MgO}-\text{FeO}-\text{SiO}_2$ (BOWEN and SCHAIERER, 1935). The mineralogy of the Holbrook chondrite suggests that these minerals originally crystallized under equilibrium conditions, and that the meteorite is not a chance aggregate of minerals of random and variable composition.

CHEMICAL COMPOSITION

The chemical analysis is given in Table 1, in the conventional form expressed as oxides, troilite, and metal; in terms of the individual elements; and recalculated on a volatile-free basis.

Some elements were determined by emission spectrography, as well as by conventional wet chemical methods. The spectrographic determinations were made in the spectrographic laboratory of the Geology Department of the University of Chicago on a sample of the Holbrook meteorite obtained from the Chicago Natural History Museum. A comparison of the two sets of results are given in Table 2. The agreement is close except for aluminium. The figures given in Table 1 are the results of wet chemical analysis on the sample from the American Museum of Natural History.

Sodium and potassium have been determined several times in Holbrook. The results, and the methods used, are set out in Table 3.

Table 1. Chemical analysis of the Holbrook meteorite

(A)		(B)		(C)	
Fe	7.18	H	0.029	Na	1.14
Ni	1.09	C	0.06	Mg	25.07
Co	0.052	O	36.471	Al	1.65
Cu	0.0096	Na	0.69	Si	30.95
FeS	7.94	Mg	15.18	P	0.28
SiO ₂	40.11	Al	1.00	K	0.13
TiO ₂	0.14	Si	18.74	Ca	2.05
Al ₂ O ₃	1.90	P	0.17	Ti	0.13
Cr ₂ O ₃	0.45	S	2.90	Cr	0.58
FeO	12.01	K	0.08	Mn	0.48
MnO	0.37	Ca	1.24	Fe	35.61
MgO	25.18	Ti	0.08	Co	0.087
CaO	1.74	Cr	0.31	Ni	1.80
					99.95
Na ₂ O	0.93	Mn	0.29		
K ₂ O	0.10	Fe	21.56		
P ₂ O ₅	0.40	Co	0.052		
H ₂ O+	0.27	Ni	1.09		
C	0.06	Cu	0.0096		
	99.99		99.99		

(A) Chemical analysis expressed as nickel-iron, troilite and oxides (all H as H₂O, all C as C (both free and combined)).

(B) Chemical analysis expressed as elements, with calculated figure for oxygen.

(C) Chemical analysis recalculated on a volatile-free (O, C, S, H) basis.

Table 2. Comparison of results of (A) spectrographic analysis of a sample of Holbrook from the Chicago Natural History Museum and (B) wet chemical analysis of a sample of Holbrook from the American Museum of Natural History

	(A)	(B)
	(%)	(%)
Co	0.054	0.052
Ni	1.01	1.09
Ti	0.06	0.08
Al	1.27	1.00
Mn	0.28	0.29
Cr	0.35	0.31
	(p.p.m.)	
V	98	—
Cu	96	—
Sc	7.4	—
Y	2.3	—

The normative mineral composition, expressed as weight percentages, is given in Table 4. This has been calculated as suggested by WAHL (1950b), except that we prefer to calculate P₂O₅ as apatite, not merrillite; the composition of merrillite is

Table 3. Sodium and potassium determinations on the Holbrook meteorite

Na	K	Method used
0.58	0.13	Lawrence Smith, K precipitated as K_2PtCl_6 (WAHL, 1950b)
0.69	0.08	Lawrence Smith, K precipitated as $KB(C_6H_5)_4$ (this paper)
—	0.08	Emission spectrography (AHRENS <i>et al.</i> , 1952)
0.73	0.087	High-temperature distillation, followed by flame photometry (EDWARDS and UREY, 1955)

not well established, being based on a single analysis of a small amount of impure material, and this mineral may well be a variety of apatite.

It should be emphasized that the normative mineral composition calculated from the chemical analysis can only approximate the actual mineralogy of the meteorite. The calculation involves several arbitrary procedures. Alumina is calculated entirely as feldspar, although it is known that small amounts are present in pyroxene (an analysis, MASON and WILK, 1960, of orthorhombic pyroxene from the Miller, Arkansas, chondrite shows 1.22 per cent Al_2O_3). The TiO_2 is calculated as ilmenite, but the titanium is present wholly or in large part in the ferromagnesian minerals, pyroxene and olivine. The calculation assumes that the Fe/Mg ratio is the same in all the ferromagnesian minerals, but measurements of the optical properties of these minerals show that this is not the case. Nevertheless, when interpreted with care and discrimination, the normative mineral composition provides a useful guide to the actual mineral composition, and conversely the actual mineral composition can be most readily correlated with the chemical composition through the calculated norm.

Table 4. Normative mineral composition of the Holbrook meteorite

	%
Nickel-iron	8.33
Troilite	7.94
Olivine	37.63
Hypersthene	30.16
Diopside	4.27
Orthoclase	0.62
Albite	7.86
Anorthite	0.70
Apatite	0.94
Chromite	0.76
Ilmenite	0.25

The normative mineral composition of the Holbrook meteorite correlates well with the observed mineral composition. As mentioned previously, apatite was not observed but is presumably present. The small amount of titanium is probably not present as ilmenite, but in the silicate phases (the analysis of pyroxene from the

Miller, Arkansas, chondrite shows 0.21 per cent TiO_2). The potassium is almost certainly in solid solution in the plagioclase phase. The calculated diopside is in the hypersthene phase. Assuming the compositions for the olivine and pyroxene deduced from optical and X-ray measurements, the percentage of MgO would be 24.6 (against 25.18 actually determined) and FeO would be 13.0 (against 12.01 actually determined, to which the 0.37 per cent MnO should be added). The agreement between these figures is satisfactory.

The chemical analysis shows that the Holbrook stone, according to the classification of PRIOR (1920) falls into his group of hypersthene-olivine chondrites. According to the classification of UREY and CRAIG (1953), it belongs to their L group, since it contains low total iron (21.56 per cent, the average for the L group being 22.33 per cent). Holbrook is closely comparable chemically and mineralogically with a number of hypersthene-olivine chondrites, including Monte das Fortes, Linum, Varpaisjärvi, and McKinney (WILK, 1956), Launton (PRIOR, 1916), Crumlin (FLETCHER, 1921), and Gudder (JEREMINE and SANDREA, 1953).

MINOR AND TRACE ELEMENTS

Probably on account of its wide distribution and thus its availability, Holbrook has been used for many determinations of minor and trace elements in meteoritic material. We have attempted to collect as many of these determinations as possible and they are presented below.

Barium: 9 p.p.m. (PINSON *et al.* 1953; by emission spectrography); 3.6 p.p.m. (REED *et al.*, 1960; by neutron activation).

Bismuth: 0.0021 p.p.m. (EHMANN and HUIZENGA, 1959; by neutron activation); 0.002–0.0075 p.p.m. (REED *et al.*, 1960; by neutron activation).

Caesium: 0.49 p.p.m. (GORDON *et al.*, 1957; by isotope dilution); 0.283 p.p.m. (WEBSTER *et al.*, 1958; by isotope dilution); 0.146 p.p.m. (GAST, 1960; by isotope dilution).

Chromium: 3500 p.p.m. (this paper; by emission spectrography); 3100 p.p.m. (this paper; by wet chemical analysis); 2150 p.p.m. (BATE *et al.*, 1960; by neutron activation).

Copper: 96 p.p.m. (this paper; by emission spectrography).

Europium: 0.081 p.p.m. (BATE *et al.*, 1960; by neutron activation).

Indium: 0.001 p.p.m. (SCHINDEWOLF and WAHLGREN, 1960; by neutron activation).

Lead: 0.3–0.5 p.p.m. (MARSHALL and HESS, 1958; by isotope dilution); 0.3–0.6 p.p.m. (REED *et al.*, 1960; by neutron activation).

Lithium: 3.3 p.p.m. (PINSON *et al.*, 1953; by emission spectrography).

Mercury: 0.052 p.p.m.- Hg^{202} (EHMANN and HUIZENGA, 1959; by neutron activation).

Rhodium: 0.15 p.p.m. (SCHINDEWOLF and WAHLGREN, 1960; by neutron activation).

Rubidium: 8 p.p.m. (PINSON *et al.*, 1953; by emission spectrography); 2.3 p.p.m. (WEBSTER *et al.*, 1958; by isotope dilution); 2.22 p.p.m. (GAST, 1960; by isotope dilution).

Scandium: 8.5 p.p.m. (PINSON *et al.*, 1953; by emission spectrography); 7.4

p.p.m. (this paper; by emission spectrography); 9.7 p.p.m. (BATE *et al.*, 1960; by neutron activation).

Selenium: 13.3 p.p.m. (SCHINDEWOLF, 1960; by neutron activation).

Silver: 0.04 p.p.m. (SCHINDEWOLF and WAHLGREN, 1960; by neutron activation).

Strontium: 13 p.p.m. (PINSON *et al.*, 1953; by emission spectrography); 12 p.p.m. (GAST, unpublished).

Tellurium: 0.62 p.p.m. (SCHINDEWOLF, 1960; by neutron activation).

Thallium: 0.0004–0.0038 (REED *et al.*, 1960; by neutron activation).

Thorium: 0.038 p.p.m. (BATE *et al.*, 1959; by neutron activation).

Uranium: 0.014 p.p.m. (HAMAGUCHI *et al.*, 1957; by neutron activation).

Vanadium: 98 p.p.m. (this paper; by emission spectrography).

Yttrium: 2.3 p.p.m. (this paper; by emission spectrography).

Zirconium: 28 p.p.m. (PINSON *et al.*, 1953; by emission spectrography).

Note added in proof:—Determination of the noble metals by cupellation followed by emission spectrography (analysts: A. LÖFGREN, P. VÄÄNÄNEN and H. B. WIIK) gave the following results (all in p.p.m.): Ru 0.060; Rh 0.064; Pd 0.44; Os 0.16; Ir 0.24; Pt 0.44; Au 0.04.

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Einbau von Bor in detritische Tonminerale

Experimente zur Erklärung des Borgehaltes toniger Sedimente

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Abstract—Geochemical research had shown that the high concentrations of boron of clay sediments are attributable to the illites. These contents of boron are either due to later absorption from the seawater or to new formation of micas with simultaneous installation of boron.

Having treated clays poor of boron with solvents containing boron, it could be shown by experiment that clays can take boron from the solvents. The absorbed quantities of boron depend on the duration of treatment, on temperature, on concentration of boron, on pH of the solvents and on the mineralogical composition of the investigated clays. Dioctahedral micas absorb more boron than the further clay minerals as Kaolinite, Montmorillonite and others.

Since boron practically cannot be washed away and since there is no adjustment of chemical equilibrium even after a longer treatment, adsorption cannot exist and it is to suppose that an installation of cations of boron into the lattice of mica takes place. It is probable that boron replaces the aluminium resp. the silicon in the tetrahedral position.

Through these experiments it is likely that illites mostly are concerned as relics of weathering and to a less degree as new formations.

1. PROBLEMSTELLUNG

SEIT den Untersuchungen von GOLDSCHMIDT und PETERS (1932) ist bekannt, dass marine Tone sehr reich an Bor sind. GOLDSCHMIDT stellte daher das Bor zu den thalassophilen Elementen. LANDERGREN (1945) baute diese Ergebnisse aus und glaubte, dass eine direkte Beziehung zwischen Borgehalt der Sedimente und Salinität des Meerwassers, in dem das Sediment zur Ablagerung kam, besteht. LANDERGREN und auch GOLDSCHMIDT deuteten diese erhöhten Borgehalte der marinen Sedimente durch eine Adsorption von Borat-Ionen an die Tone. GOLDBERG und ARRHENIUS (1958) wandten jedoch ein, dass der grösste Teil des Bors fest an die Tonminerale gebunden und nicht auszuwaschen ist, eine Tatsache, die durch die Untersuchung des Verfassers (HARDER, 1959) bestätigt worden ist. Da eine Adsorption ausscheidet, deutete ARRHENIUS diesen Befund als einen Beweis für die diagenetische Neubildung der Tonminerale im Sediment. Vom Verfasser konnte durch geochemische Untersuchungen an reinen Mineralen, an magmatischen Gesteinen und auch an Sedimenten gezeigt werden, dass das Bor in den Gesteinen zum grössten Teil an die hellen muskovitischen Glimmer gebunden ist. Falls die Theorie von ARRHENIUS richtig ist, wären daher auch die Illite als rein diagenetische oder autigene Neubildung im Sediment zu deuten.

Schwer zu deuten blieb jedoch die Tatsache, dass aus einer verdünnten NaCl-Lösung, die das Meerwasser ja darstellt, sich nur kalihaltige und nicht natriumhaltige (Paragonit) Glimmer bildeten (HARDER, 1956). Als Erklärung für das Nichtauftreten des Paragonits könnte jedoch angenommen werden, dass das grosse Kalium (1,33 Å) besser in die Zwölferkoordination der Alkalien in den Glimmern passt als das kleine Natrium (0,98 Å). Gegen diese Theorie der Neubildung der Illite ergaben aber auch die geochemischen Untersuchungen von

Tonen aus verschiedenen Ablagerungen einige wesentliche Widersprüche. So sprachen z.B. das geologische Vorkommen der schnellsedimentierten Salztone (bis 2000 g B/t) oder auch die grobblättrigen Muskovite aus dem Buntsandstein, die auch sehr viel Bor enthalten, gegen eine Neubildung. Weiter waren viele andere Beobachtungen mit der diagenetischen Neubildung der Illite, die neuerdings von vielen Seiten geäußert wird, nicht in Übereinstimmung zu bringen, sondern erklärten sich einfacher, wenn man die Illite als Verwitterungsreste der Glimmer ansah. Diese Vorstellung hat CORRENS in seinen Vorlesungen und Veröffentlichungen seit langem vertreten; wobei auch CORRENS die Neubildung von Illit in speziellen Fällen nicht für unmöglich hält, jedoch glaubt, dass die Verwitterungsreste in den Illiten vorherrschen.

Für die Beantwortung dieser Frage ob es sich bei den Illiten um Verwitterungsreste oder um diagenetische Neubildungen im Meerwasser handelt wären Versuchsergebnisse von Interesse.

2. BESCHREIBUNG DER EXPERIMENTE

Um dieser Frage nachzugehen, mussten borarme Sedimente mit borreichen Lösungen behandelt werden. Da durch geochemische Untersuchungen gezeigt wurde, dass der Borgehalt der tonigen Fraktionen fast ausschliesslich an die feinkörnigen muskovitischen Glimmer der Sedimente, die sog. Illite, gebunden ist, wäre es am sinnvollsten gewesen, reine borarme Illite der Behandlung mit Borsäure auszusetzen. Leider waren aber reine borarme Illite nicht aufzufinden. Illit aus dem Muschelkalk Göttingens enthielt, wenn er aus Kalken isoliert war, 210 g B/t; wenn er aus Dolomitbänken des Muschelkalkes stammte, sogar 300 g B/t. Die amerikanischen Illitproben Morris, Illinois, $\phi < 2 \mu$, 325 g B/t, und Fithiam, Illinois, 210 g B/t, ergaben ebenso hohe Werte. Die Proben mit den hohen Borgehalten waren ungeeignet, da eine Aufnahme von Bor sicher langsam vor sich geht und auch analytisch eine Zunahme von z.B. 20 g B/t bei borreichem Material schwerer zu ermitteln ist als die gleiche Zunahme bei borarmen Proben. Ein Ausweg wurde in einem borarmen ($\phi < 0,6 \mu$, 34 g B/t) Pleistozän-Ton gefunden, der neben Illit noch Chlorit enthielt. Dieser Ton hatte auch gegenüber den reinen Illiten den Vorteil, dass er den natürlichen Verhältnissen näherkam. Auf Grund der geochemischen Untersuchungen war anzunehmen, dass bei den Borkonzentrationen, wie sie im Meerwasser vorliegen, nur mit einer sehr langsamen Aufnahme von Bor zu rechnen ist. So enthalten z.B. die im Schelfbereich sedimentierten Tone im allgemeinen weniger Bor als die langsamer sedimentierten Tiefseetone. Um diesen Faktor Zeit in einem experimentell zumutbaren Rahmen zu halten, musste die Konzentration an Bor wesentlich erhöht werden. Der Pleistozän-Ton wurde daher mit einer wässrigen Lösung von Borsäure (10 g $\text{H}_3\text{BO}_3/\text{lH}_2\text{O}$) oder Natriumtetraborat (10 g $\text{Na}_2\text{B}_4\text{O}_7/\text{lH}_2\text{O}$) bei verschiedenem pH, verschiedenen Temperaturen und verschieden langen Zeiten behandelt. Um ein Absedimentieren des Tones zu verhindern, wurden die Proben etwa während der Hälfte der Zeit in den bei sedimentpetrographischen Arbeiten üblichen Maschinen geschüttelt. Nach der Behandlungszeit wurden die Proben im Ultrafiltrationsgerät filtriert und durch etwa 20 maliges Waschen und anschliessendes Trockensaugen sehr sorgfältig von borhaltigen Lösungen befreit. Nach dieser Filtration

wurde der Ton mit destilliertem Wasser erneut aufgeschüttelt und zur Abtrennung der Fraktion $\phi < 0,6 \mu$ nach dem Atterberg-Verfahren einer grossen Menge destillierten Wassers (ca. 10 l.) ausgesetzt. Nach Absitzen der gröberen Teilchen wurde je nach Fallhöhe nach 1–2 Wochen die Fraktion $\phi < 0,6 \mu$ abgetrennt, ultrafiltriert, mehrmals sorgfältig gewaschen und das Bor in der Fraktion spektral-analytisch mit BeO als innerer Standard (HARDER, 1959) bestimmt.

3. VERSUCHSERGEBNISSE AN EINEM PLEISTOZÄNEN TON

Die Versuche ergaben, dass eine Aufnahme von nicht auswaschbarem Bor aus der Lösung stattgefunden hat. Die Aufnahme des Bors wurde—wie schon gesagt—in Abhängigkeit von der Behandlungszeit, vom pH, der verschiedenen Art der Bor-Ionen und der Temperatur untersucht.

Die aufgenommene Bormenge in der Abhängigkeit von der Zeit ergibt sich aus den folgenden Zahlen: Bänderton von Nyland, Schweden, 34 g B/t behandelt

(a) Mit Borsäure (10 g $\text{H}_3\text{BO}_3/\text{lH}_2\text{O}$)

Dauer der Behandlung	Ionen	pH	Gehalt nach der Behandlung (g B/t)	Zunahme an Bor (g B/t)
(1) 1,5 Stunden	$\text{H}_3\text{BO}_3 + \text{NH}_4\text{OH}$	7,35	48	14
(2) 35 Tage	$\text{H}_3\text{BO}_3 + \text{NH}_4\text{OH}$	7,4	56	22
(3) 153 Tage	$\text{H}_3\text{BO}_3 + \text{NH}_4\text{OH}$	7,8	80	46

(b) Mit Natriumtetraborat (10 g $\text{Na}_2\text{B}_4\text{O}_7/\text{lH}_2\text{O}$)

Dauer der Behandlung	Ionen	pH	Gehalt nach der Behandlung (g B/t)	Zunahme an Bor (g B/t)
(4) 3 Tage	$\text{Na}_2\text{B}_4\text{O}_7 + \text{H}_3\text{BO}_3$	7,4	65	31
(5) 35 Tage	$\text{Na}_2\text{B}_4\text{O}_7 + \text{HCl}$	7,45	75	41

Die Zunahme des Borgehaltes der Borfraktionen ist in den ersten Stunden der Behandlung sehr hoch und sinkt im Laufe der Zeit stark ab. So wurden beim Behandeln mit Borsäure in den ersten $1\frac{1}{2}$ Stunden bereits 14 g B/t aufgenommen, während nach 35 Tagen nur eine Zunahme von insgesamt 22 g B/t ermittelt wurde. Das bedeutet, dass in der rund 500 mal längeren Zeit die weitere Zunahme nur 8 g B/t betrug. Ein Gleichgewicht im Borgehalt des Tones und der Borkonzentration der Lösungen war auch nach einer halbjährigen Behandlung noch nicht erreicht. Auch beim Natriumtetraborat liess sich eine Zunahme an Bor mit der Dauer der Behandlung feststellen.

(c) Bei verschiedener Wasserstoffionenkonzentration

Die Abhängigkeit des aufgenommenen Bors vom pH wurde dann untersucht. Um neutrale Lösungen zu erhalten, wurde zu der sauren Lösung der Borsäure NH_4OH zugefügt und zu der basischen des Natriumtetraborats etwas HCl. Verwandt wurde für diese Versuche auch wieder der Ton von Nyland, Schweden, 34 g B/t.

Dauer der Behandlung	Ionen	pH	Gehalt nach der Behandlung (g B/t)	Zunahme an Bor (g B/t)
(6) 35 Tage	H_3BO_3	3,5	65	31
(7) 35 Tage	$\text{H}_3\text{BO}_3 + \text{NH}_4\text{OH}$	7,4	56	22
(8) 35 Tage	$\text{Na}_2\text{B}_4\text{O}_7 + \text{HCl}$	7,45	75	41
(9) 35 Tage	$\text{Na}_2\text{B}_4\text{O}_7$	8,9	54	20

Während der Versuche, die in Polyäthylenflaschen durchgeführt wurden, änderten sich die pH-Werte nur unwesentlich. Die Abhängigkeit vom pH für die Aufnahme des Bors ist nicht sehr gross und ausserdem nicht einheitlich. Es sieht vielmehr so aus, als ob die Art der Bor-Ionen oder die Fremdionen (hier Na) von grösserem Einfluss für die Aufnahme von Bor sind. Natriumtetraborat-Ionen sind anscheinend besser geeignet, von den Tönen aufgenommen zu werden als Ionen der Borsäure; ein Ergebnis, das sich auch bei den folgenden beschriebenen Versuchen immer wieder bestätigte. So ergibt sich z.B. eine Zunahme von 41 g B/t bei Behandlung von $\text{Na}_2\text{B}_4\text{O}_7$, während sich beim gleichen pH bei H_3BO_3 nur eine Zunahme von 22 g B/t feststellen lässt. Dieses Ergebnis lässt sich nicht allein durch die etwas höhere Borkonzentration im Natriumtetraborat (2,13 g B/1H₂O) im Vergleich zur Borsäure (1,76 g B/1H₂O) erklären, sondern ist möglicherweise auf die Fremdionen zurückzuführen. Sowohl bei der Borsäure als auch beim Natriumtetraborat scheinen saure pH-Bedingungen für die Aufnahme von Bor günstiger zu sein.

(d) *Bei erhöhter Temperatur*

Wie bei allen chemischen Reaktionen war auch bei diesen Versuchen eine Abhängigkeit von der Temperatur zu erwarten. Die bisher beschriebenen Versuche waren bei der relativ konstanten Kellertemperatur (im Mittel von etwa 15°C) ausgeführt worden. Lediglich bei dem über 135 Tage laufenden Versuch Nr. (3) traten grössere Schwankungen auf. Versuche bei erhöhten Temperaturen wurden mit dem gleichen Ton im Trockenschrank bei 80°C durchgeführt. Bei diesen Versuchen konnten die Proben jedoch nicht geschüttelt werden.

Dauer der Behandlung	Ionen	pH	Gehalt nach der Behandlung (g B/t)	Zunahme an Bor (g B/t)
(10) 23 Tage	H_3BO_3	3,8*	169	135
(11) 23 Tage	$\text{H}_3\text{BO}_3 + \text{NH}_4\text{OH}$	6,8	144	110
(12) 23 Tage	$\text{Na}_2\text{B}_4\text{O}_7 + \text{HCl}$	7,9	209	175

* Am Ende dieses Versuchs wurde ein pH von 5,0 festgestellt (Auslaugung des Alkali aus der Glasflasche die aus Sicherheitsgründen verwandt wurde). Bei allen anderen Versuchen blieb das pH etwa gleich hoch.

Vergleicht man das in der letzten Zeile angegebene Versuchsergebnis (12) mit dem im Vorhergehenden besprochenen Versuch (8), so ergibt sich, dass bei 80°C 4 bis 5 mal mehr Bor eingebaut worden ist als bei den niedrigeren Temperaturen

von 15°C. Bei den noch niedrigeren Temperaturen des Meerwassers (Tiefenwasser etwa 4°C) müssen wir etwa mit halb so hohen Werten rechnen, wie sie bei den Versuchen um 15°C ermittelt wurden.

Die Menge des eingebauten Bors war abhängig von der Dauer und der Temperatur der Behandlung. Versucht man nun, aus den Versuchsergebnissen abzuschätzen, wie lange es dauert, bis aus einem borarmen limnischen Ton ein Ton mit etwa 300 g B/t wird (für die Fraktion $\phi < 0,6 \mu$), so muss man als wesentlich unterschiedliche Faktoren die niedrigere Temperatur und vor allem den grössenordnungsmässig geringeren Borgehalt des Meerwassers in Rechnung setzen. Derartige Abschätzungen sind natürlich mit grösster Vorsicht zu behandeln, da bei den Experimenten wesentliche Vereinfachungen, z.B. das Nichtberücksichtigen der Fremdionen (vorwiegend NaCl), angewandt werden mussten.

Die Gehalte der Borsäurelösungen sind beim Natriumtetraborat etwa 450 mal höher, bei der Borsäure etwa 370 mal höher als die Borgehalte des Meerwassers, die im Mittel mit 4,8 mg B/l. Meerwasser angegeben werden können. Ausser dem Konzentrationseinfluss, der aber wahrscheinlich nicht linear eingeht, ist vor allem abzuschätzen, wie schnell bzw. besser, wie langsam sich die Boraufnahme mit der Zeit verändert. Unter plausiblen Annahmen ergibt sich für die Zunahme des Borgehalts der Fraktion $\phi < 0,6 \mu$ auf 300 g B/t ein Zeitraum von mehreren 10 000 Jahren. Bei erhöhten Temperaturen und vor allem bei erhöhten Borkonzentrationen, mit denen man z.B. im Zechstein in einigen Nebenbecken rechnen muss, wird diese Zeit wesentlich kürzer sein.

4. VERSUCHSERGEBNISSE

(a) *Mit Montmorillonit und Kaolinit*

Alle bisher beschriebenen Versuche waren durchgeführt worden mit einem Ton, der mehrere Minerale enthielt. Es war stets dabei angenommen worden, dass das Bor vorwiegend vom Illit aufgenommen wurde, ohne dabei schon zu diskutieren, ob es sich um eine Adsorption an die Tone handelt, oder welcher andere Vorgang vorliegt. Ein Beitrag für die Beantwortung dieser Frage wurde erhofft von dem Ergebnis der Behandlung anderer Tonminerale mit borhaltigen Lösungen, vor allem von Tonmineralen, die bei Behandlung mit Alkali-Ionen ein grosses bzw. ein mittleres Austauschvermögen haben, z.B. vor allem vom Montmorillonit und Kaolinit. Ein röntgenographisch reiner Kaolin vom Westerwald, Deutschland, und ein Montmorillonit von Polkville, Mississippi, U.S.A., wurden mit $\text{H}_3\text{BO}_3 + \text{Na}_2\text{B}_4\text{O}_7$ (10 g/l. H_2O) bei neutralem pH (etwa 7) während 30 Tage der gleichen Behandlung unterworfen wie der Ton von Nyland.

Das Ergebnis zeigt, dass im Vergleich zu den illithaltigen Proben nur ein Bruchteil an Bor von den Montmorillonit- und Kaolinit-Tonen aufgenommen worden ist bzw., dass die schwach adsorbierten Ionen an der Tonoberfläche durch das Waschen praktisch vollständig entfernt wurden. Das Bor wird also, wie auch die Experimente zeigen, spezifisch von den hellen, dioktaedrischen Illiten aufgenommen und nicht von den anderen Tonmineralen. Wie liegt nun das Bor in den Glimmern vor? Handelt es sich um eine Adsorption oder ist eine festere Bindung zustande gekommen? In den Versuchen mit dem Ton von Nyland war

(13) Montmorillonit Polkville, Mississippi, U.S.A.	Borgehalt in der Fraktion $\phi < 0,6 \mu$		g B/t
		vor der Behandlung	6
		nach der Behandlung	9,3
(14) Kaolinit Westerwald, Deutschland	Borgehalt in der Fraktion $\phi < 0,6 \mu$	Zunahme während der Behandlung	3,3
		vor der Behandlung	10,5
		nach der Behandlung	15
		Zunahme während der Behandlung	4,5

das Bor nicht auswaschbar. Diese Feststellung wird durch geochemische Untersuchungen an natürlichen Tonen noch unterstrichen. So konnte z.B. bei der Untersuchung von Pleistozän-Tonen, die durch Umlagerung aus sehr borreichen Röttonen (schwankend zwischen 300 bis 500 g B/t) entstanden sind, gezeigt werden, dass der Borgehalt bei der Umlagerung in Süßwasser während geologischer Zeiten nur unwesentlich herabgesetzt wird. In der feinsten Fraktion eines Tones, der in der Elster-Eiszeit zur Ablagerung gelangte, wurde 360 g B/t gefunden. Auch im Material, das im Cromer-Interglacial, also bei höheren Temperaturen sedimentierte, wurde noch 220 g B/t gefunden. Diese Zahlen zeigen, dass die Zeit während der Umlagerung der Röttone nicht ausgereicht hat, um Tone mit einem hohen Borgehalt in solche mit einem niedrigen Borgehalt umzuwandeln. Der Borgehalt der Süßwassertone ist in geologischen Zeiten nicht wesentlich herabgesetzt worden. Das Bor ist also nicht auswaschbar, wie man es auch auf Grund der Experimente vermutet hat. Läge nämlich eine lockere Adsorption der Borat-Ionen an der Oberfläche der Tonminerale vor, so müssten sich diese Ionen durch langes Waschen wieder entfernen lassen, wie es z.B. bei an Tonen adsorbier-ten Alkali-Ionen der Fall ist. Auch durch Behandlung der Tone, die während der Experimente Bor aufgenommen haben, mit Na_2SO_4 , AlCl_3 , HCl etc., liess sich der Borgehalt der illithaltigen Tone praktisch nicht herabsetzen.

Ein weiterer Beweis dafür, dass es sich bei der Aufnahme von Bor um eine festere Bindung und nicht um eine Adsorption handelt, kann aus der Tatsache ersehen werden, dass sich bei der Behandlung von Tonen in den Versuchen bis zu 153 Tagen kein Gleichgewicht eingestellt hat. Bei Adsorption stellt sich, wie durch FREUNDLICH bekannt ist und wie es erst neuerdings wieder durch HEYDEMANN bestätigt werden konnte, in wenigen Minuten ein Gleichgewicht ein. *Ausserdem sprechen auch die bei höheren Temperaturen aufgenommenen grösseren Bormengen gegen eine Adsorption, da nach der Langmuirschen Formel die Adsorption mit steigender Temperatur abnimmt.*

(b) Mit Muskovit

Alle diese Tatsachen deuten darauf hin, dass eine wesentlich festere Bindung vorliegen muss und dass wir wahrscheinlich mit einer chemischen Reaktion (Chemosorption) bzw., richtiger ausgedrückt, mit einem Einbau von Bor in das Gitter der dioktaedrischen Illite während der Behandlung rechnen müssen. Chemische Analysen derartiger Illite ergeben stets einen Unterschuss an einigen Elementen, vorwiegend an Alkalien. Es handelt sich um unvollständige Glimmer, wie sie

von CORRENS bezeichnet werden. Es ist begreiflich, dass die Gitter dieser unvollständigen Mineralien, die meist noch röntgenographisch schlecht geordnete Gitter aufweisen, für derartige Austauschversuche praedestiniert sind. Versuche mit einem grobblättrigen Muskovit von Tjurkil, Schweden, wurden zuerst nicht für sehr erfolgversprechend gehalten. Der grobblättrige Muskovit wurde vor der Behandlung, um eine Korngrösse von $\phi < 0,6 \mu$ zu erhalten, in der Kugelmühle gemahlen. Behandlung mit $\text{H}_3\text{BO}_3 + \text{NH}_4\text{OH}$ (10 g B/l. H_2O) beim pH 7,15 während 30 Tage, T 18°C:

(15) Muskovit Tjurkil, Schweden	Ausgangsgehalt nach der Behandlung Zunahme während der Behandlung	g B/t
		21 65 44

Das Ergebnis zeigt, dass auch der gutkristallisierte Muskovit, der allerdings vor der Behandlung gemahlen wurde, in der Lage ist, grössere Mengen von Bor aufzunehmen.

5. ZUM STRUKTURELLEN EINBAU DES BORS IN DEN GLIMMERN

Fragen wir uns nun, an welcher Stelle das Bor in den Illiten untergebracht ist.

Da die Tonminerale nur negative Überschussladungen haben, scheidet eine Aufnahme von Borat-Ionen aus. Aus räumlichen Gründen können die grossen Anionen auch nicht in Gitterplätze des Muskovits aufgenommen werden. Wir müssen so damit rechnen, dass *Bor-Kationen in das Gitter der Glimmer eingebaut worden sind*. Diese Annahme erhält durch die Tatsache, dass in sauren Lösungen mehr Bor eingebaut wird eine grössere Wahrscheinlichkeit. Das Bor ist ähnlich wie das homologe Aluminium, ein amphoter Element, d.h., es ist befähigt, sowohl als Kation wie als auch Anion aufzutreten. Beim Bor liegt aber in Lösungen dieses Gleichgewicht völlig auf der Seite der Anionen. In sauren Lösungen werden aber die B^{3+} -Ionen häufiger sein als in basischen Lösungen. Die sowohl bei dem Natriumtetraborat als auch bei Borsäurelösungen zu beobachtende Tatsache, dass saurere Lösungen mehr Bor aufnehmen, findet so eine Erklärung. Ob diese Bor-Kationen aus der Lösung direkt stammen, oder ob sie an der Grenzfläche Bor-Lösung Glimmer entstanden sind, ist nicht zu klären. Auf Grund des geringen Ionen-Radius des Bor-Kations (0,23 Å) kommen für den Einbau nur Gitterplätze mit einer geringen Koordination in Frage. Wahrscheinlich wird das dreiwertige Aluminium- (0,51 Å) oder das vierwertige Si- (0,42 Å) Ion vom Bor in den Tetraederpositionen vertreten.

An welchen Gitterpositionen das Bor in den Glimmern untergebracht ist, ist schwer zu entscheiden, da röntgenographisch so geringe Unterschiede nicht nachzuweisen sind. Ein Hinweis, wo das Bor eingebaut ist, kann vielleicht aus der Tatsache abgeleitet werden, dass Illit Bor einbaut, während es bei Kaolinit und Montmorillonit nicht festzustellen ist. Die Muskovitstruktur unterscheidet sich von der Kaolinit- und Montmorillonitstruktur dadurch, dass sie Aluminium

in der Tetraederposition eingebaut hat, während dies bei den meisten Montmorilloniten und beim Kaolinit nur im geringen Umfang der Fall ist. Auch die Chlorite, die Bor enthalten, wenn auch weniger als die Glimmer, haben Aluminium formelmässig in die Tetraederposition eingebaut, so dass diese Erklärung allgemein nicht stichhaltig ist.

Nehmen wir aber—mit den genannten Einschränkungen—als richtig an, dass das Bor das Aluminium in den Tetraederpositionen ersetzt, so wäre interessant zu wissen, wieviel Prozent dieser Al-Positionen durch Bor ersetzt sind. Wären alle Tetraederpositionen des Al durch B getarnt, so würde dieser Glimmer 2,9% Bor enthalten. In einigen Salztönen (Fraktion $\phi < 0,6 \mu$) sind aber höchstens 2000 g B/t (0,2% B), also nur rund 1/10 des maximal möglichen Wertes nachgewiesen worden. Würde das gesamte Bor dieses Salztöns nur die äusseren möglichen Positionen belegen, so wären die fünf oberen und unteren Tetraederschichten des Blättchens mit Bor anstelle von Aluminium belegt. Bei den Experimenten wurde wesentlich weniger Bor eingebaut, meistens nur 30 g B/t. Der höchste Wert liegt bei 209 g B/t (Versuch 12), also nur der zehnte Teil des Wertes der Salztöne.

In den Versuchen ist so lediglich ein Teil der Al-Positionen der äusseren Tetraederschicht durch Bor ersetzt worden. Die Tatsache, dass sich die Aufnahme von Bor mit der Dauer der Behandlung sehr verlangsamt, wird durch die Besetzung der leicht zugänglichen äusseren randlichen Positionen mit Bor verständlich.

6. ERKLÄRUNG DER GEOCHEMISCHEN VERTEILUNG DES BORS IN DEN TONIGEN SEDIMENTEN

Die beschriebenen Experimente erklären die an natürlichen Tönen in der geochemischen Verteilung des Bors zu beobachtenden Erscheinungen.

Nach den geochemischen Untersuchungen (HARDER, 1959) ist der Borgehalt toniger Sedimente abhängig von dem Mineralbestand, der Korngrösse, der Temperatur und vor allem der Salzkonzentration (Borgehalt des Wassers) und nicht zuletzt von der Herkunft des Materials und der Ablagerungsgeschwindigkeit. Beim Vergleich des Mineralbestandes mit dem Borgehalt zeigte sich, dass illitreiche Sedimente grössenordnungsmässig mehr Bor enthalten als illitfreie; eine Tatsache, die sich einfach durch die Fähigkeit eines nachträglichen Einbaus von Bor in die Glimmer erklärt.

Die Abhängigkeit des Borgehaltes von der Korngrösse ist nicht nur auf eine andere mineralogische Zusammensetzung, z.B. durch die Zunahme des Quarzes, zurückzuführen, sondern findet ihre einfache Erklärung durch den verschiedenen starken Einbau von Bor in die Illite verschiedener Korngrösse. Die feinkörnigen Proben haben eine grössere Oberfläche und bauen so unter gleichen Bedingungen und gleicher Zeit mehr Bor ein als die grobkörnigen Fraktionen. So findet man z.B. in den Illiten von Fithian, Illinois, U.S.A., die kleiner als $2 \mu (\phi < 2 \mu)$ sind, 210 g B/t, während in den Fraktionen, die gröber als $2 \mu (\phi > 2 \mu)$ sind, mit 130 g B/t etwa nur die Hälfte nachgewiesen wurde. Konzentrationsunterschiede an Bor in den Lösungen, aus denen die Tone zur Ablagerung gelangten, erklären die grössenordnungsmässig unterschiedlichen Gehalte der Salztöne (bis 2000 g B/t in der Fraktion $\phi < 0,6 \mu$), in den marinen Tönen (einige 100 g B/t) und in den reinen limnischen Tönen noch wesentlich weniger. Während der Bildung der

Salztone des deutschen Zechsteins müssen wir mit wesentlich höheren Borgehalten im Wasser der Meeresbecken, in denen die Salze und auch die Salztone zur Ablagerung gelangten, rechnen. Ausserdem wird die erhöhte Temperatur, die man während des Zechsteins und auch des Buntsandsteins annimmt, die Ausbildung der Tone mit den extrem hohen Borgehalten begünstigt haben, wie sich aus den Experimenten ergibt.

Die Abhängigkeit der Höhe des Borgehaltes von der Herkunft des Materials zeigte sich recht gut bei den limnischen Sedimenten. Bei den limnischen Tönen leitet sich der Borgehalt vor allem aus dem Material her, aus dem die Sedimente entstanden sind. Bei dem pleistozänen Material erklärt sich der niedrige Gehalt der schwedischen Diluvialtone (um 30 g B/t) aus dem Borgehalt der hellen Glimmer, der magmatischen und metamorphen Gesteine, während der höhere Borgehalt der pleistozänen Tone aus dem Göttinger Raum (bis 220 g B/t) auf die Buntsandsteintone zurückzuführen ist (siehe HARDER, 1959, S. 131 ff.). Die Dauer der Einwirkung des borhaltigen Meerwassers auf die umgelagerten Tone erklärt die Tatsache, dass die Schelfsedimente weniger Bor enthalten als die Tiefseetone des Atlantiks (um 200 g B/t) und vor allem des Pazifischen Ozeans (im Mittel 300 g B/t, nach GOLDBERG und ARRHENIUS, 1958). Die wesentlich geringere Sedimentationsgeschwindigkeit im Pazifik im Vergleich zum Atlantischen Ozean erklärt die deutlich höheren Borwerte dieser Tiefseesedimente.

7. ZUR BILDUNG DER ILLITE

Die Entstehung der Illite erscheint durch die Experimente in einem neuen Licht. Für die Bildung der Illite werden im wesentlichen drei verschiedene Theorien angenommen: (1) reine diagenetische Neubildung im Sediment, (2) Umbau von Montmorillonit unter Aufnahme von Kalium und (3) Illit als ein Verwitterungsrest von verschiedenen Glimmern (CORRENS 1933).

Als Neubildung von Glimmern werden sicherlich zu Recht Blättchenaggregate angesehen, wie sie zum Beispiel von NORIN (1953) in sandigen Sedimenten des Thyrrenischen Meers beschrieben worden sind. Man verallgemeinerte derart spezielle Bildungen und glaubte, dass es sich bei allen Illiten um Neubildungen handelte. Bei der Untersuchung von Tiefseetonen konnte von CORRENS und von LOCHER (1952) keine Änderung der Zusammensetzung der Tonminerale mit zunehmender Sedimenttiefe festgestellt werden. Eine allgemeine Neubildung von Illiten nach der Ablagerung (Diagenese) findet also nicht statt. Man glaubte daher, dass die Neubildung der Illite unmittelbar bei der Ablagerung oder sogar im Meerwasser stattfände. Als einen geochemischen Beweis für die Neubildung der Tonminerale im Meerwasser wurde der erhöhte Borgehalt in den tonigen Sedimenten angesehen (ARRHENIUS, 1958). Die hohen Borgehalte in verschiedenen Illitablagerungen und vor allem die beschriebenen Experimente sprechen aber für einen nachträglichen Einbau von Bor in die detritischen Glimmerminerale. Ganz einwandfrei ist gezeigt worden, dass die Glimmer befähigt sind, Bor aus wässrigen Lösungen aufzunehmen. Nicht ganz sicher auszuschliessen ist jedoch die Frage, ob neben dem Einbau von Bor in die Glimmer noch im geringen Umfang eine Neubildung von Illit oder ein Umbau von anderen Mineralen mit gleichzeitigem Einbau von Bor bei der Ablagerung und der Diagenese im Sediment stattfindet. Der

verschieden hohe Borgehalt der tonigen Sedimente kann so nicht als ein Beweis für die Neubildung der Tonminerale und so auch nicht des Illits gewertet werden, sondern er spricht dafür, dass in den meisten Fällen sicherlich aller Illit als Verwitterungsrest magmatischer Glimmer oder als umgelagertes älteres Sediment zur Ablagerung gelangt ist.

8. SCHLUSSBETRACHTUNG

Die Aufnahme des Bors in die Glimmer ist von allgemeinem Interesse, da die Versuche zeigen, dass chemische Veränderungen detritischer Minerale im Meerwasser stattfinden können, die nicht, wie bei einer Adsorption, zu einer schwachen Bindung führen, sondern durch Einbau von Ionen zu bleibenden chemischen Veränderungen beitragen. Die geochemischen Veränderungen in den Illiten erfolgten durch Austausch von Ionen des Gitters gegen ein anderes Ion.

Ähnliche Veränderungen werden im Alkaligehalt der Glimmer beschrieben. So machen GRIM *et al.* (1949) wahrscheinlich, dass es bei kaliverarmten Illiten zu einer Kalifizierung kommt. Weiterhin wird von GRÜNER (1935) Kationenumtausch von Kalium gegen Thallium (bis zu 25%) angegeben.

Ob dieser Einbau von Spurenelementen auch bei Hauptbestandteilen möglich ist, bleibt abzuwarten. Wieweit zum Beispiel das Magnesium und Eisen der Oktaederschichten des Biotits über derartige Austauschreaktionen durch Aluminium zu ersetzen sind und so aus einem trioktaedrischen Glimmer der Magmasteine ein dioktaedrischer Illit gebildet wird, soll experimentell entschieden werden. Wahrscheinlich wird man damit rechnen müssen, dass derartige mit einem Einbau verbundene Austauschreaktionen eine grössere Rolle spielen als bisher angenommen wurde.

Anerkennungen—Die Untersuchungen wurden z.T. im Sedimentpetrographischen Institut der Universität Göttingen durchgeführt, wofür Herrn Prof. CORRENS aufrichtig gedankt wird. Die Deutsche Forschungsgemeinschaft förderte in dankenswerter Weise durch Sachbeihilfen die Arbeit.

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SHORT COMMUNICATION

Changes in solar luminosity and some possible terrestrial consequences

ASTRONOMERS have recently calculated in detail, the evolutionary cycle of stars such as the sun. SCHWARZSCHILD (1958) has pointed out that during the past 5 billion years, the luminosity of the sun has increased by a factor of 1.6. SCHWARZSCHILD remarks: "Can the change in brightness in the sun have had some geophysical or geological consequences that might be detectable?"

Although other factors are also involved, it is well known that the temperature at the surface of the earth is dominantly controlled by solar radiation. Other factors being equal, an increase in solar luminosity of 1.6 during geological time means that the average surface temperature of the earth has increased by 30 to 40°C over the same period. This conclusion has important climatic consequences. It implies that the average surface temperature over the earth more than approximately 3 billion years ago was below 0°C, so that most of the water on the earth would be frozen. Thus, the surface of the earth during the period between its birth, 4.5 billion years ago, and 3 billion years ago, would have passed through an intense ice age.

Under these conditions, the surface geological processes with which we are so familiar would no longer be operative. The normal geological cycle, involving weathering, erosion, transport, sorting and sedimentation, all by the action of water, would not occur. The dynamics of the crust would be radically different since the driving force for isostatic adjustment (i.e. disturbances in crustal thickness due to erosion) would be eliminated. Furthermore, the formation of sediment-filled geosynclines, the forerunners of orogeny, would be prevented. Thus the processes of metamorphism, granitization and formation of acid magmas, associated with the folding of geosynclines, would not occur.

Many geologists consider that the vast majority of granitic rocks exposed at the surface of the earth have passed through at least one normal geological cycle, and are the result of intense metamorphism and fusion of former geosynclinal sediments. Such sediments are, of course, water deposited. If this view is correct, it follows that granitic rocks with such an origin could not be formed during the period from 4.5 to 3 billion years ago.

A considerable number of age determinations have now been made on rocks from all over the world. There is a relatively complete sequence of ages from the present, ranging back to 3 billion years, but very few ages are found to be greater than 3 billion years, and none greater than 3.4 billion years. It therefore seems that a pronounced hiatus occurs in the range from 3.4 to 4.5 billion years. It is possible that rocks with ages within this range may be found, but it appears certain that they will be comparatively rare.*

The great majority of ancient dated rocks are of granitic origin. Since we have inferred that the early climatic conditions would largely prevent the formation of the common types of granites, a possible explanation for the age hiatus is apparent.

* Such rocks, if found, may have originally formed in equatorial regions where the temperature was higher than average, and sufficient to permit presence of water and the operation of normal geological processes.

In the period between 3 and 4.5 billion years, the continents may have consisted largely of basic and intermediate volcanics, formed by fractional melting in the upper mantle. Seismologists are now finding that the "intermediate layer" in continents is more widespread than formerly supposed (HALES and SACKS, 1959). The intermediate layer is thought to be essentially basaltic in composition and is separated from the sialic crust by the Conrad Discontinuity, which has been clearly located on several occasions, e.g. RICHARDS and WALKER (1959). It is interesting to speculate that the Conrad Discontinuity may be the original surface of the earth about 3 billion years ago, before the earth's temperature was warm enough to allow the normal geological cycle to operate through the agency of water.

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BOOK REVIEWS

A. A. KARTSEV, Z. A. TABASARANSKII, M. I. SUBBOTA and G. A. MOGILEVSKII: **Geochemical Methods of Prospecting and Exploration for Petroleum and Natural Gas**. English translation edited by PAUL A. WITHERSPOON and WILLIAM D. ROMY. University of California Press, Berkeley and Los Angeles, 1959. 349 pp., \$12.50.

IN THE 1930's geochemical prospecting for petroleum enjoyed a moment of popularity in America. At that time "geochemical prospecting" meant almost exclusively looking for haloes of hydrocarbons above or around petroleum-bearing structures. When it became apparent that all of the hydrocarbon anomalies (mostly methane) that were being found were produced by the decomposition of surface organic material and had no relation to petroleum, the method was abandoned with vigour. Even yet the term "geochemical prospecting" is anathema to a great many petroleum geologists in the U.S.A., even though its significance and scope are now vastly different from the original. They maintain that structures that are tight enough to hold natural gas at high pressures for tens to hundreds of millions of years are too tight to allow the escape of *any* substances; furthermore, that if small quantities of material could escape through the cap rocks the processes of diffusion are too slow to bring them to the surface in detectable amounts in geologic time.

This attitude represents an extreme point of view. The other extreme is represented by the optimistic picture painted by the book under review. Perhaps an objective evaluation of the methods would place their true usefulness somewhere in the middle. It is encouraging to note that some of the newer geochemical techniques are being investigated and employed by American companies although, for the most part, they are careful not to speak of this as "geochemical prospecting". Perhaps appearance of this book in English will encourage not only a look at new techniques, but also a reappraisal of the older ones in the light of the different approach, utilization and results reported by the Russians.

The following methods are outlined in considerable detail, with methods of application and, in some cases evaluation of the results:

- (1) Gas surveys.
 - (a) Analyses of gas in the sub-soil.
 - (b) Gas from cores.
 - (c) Gas dissolved in water.
 - (d) Gas logging of wells.
- (2) Bitumen surveys.
 - (a) By chemical analyses.
 - (b) By fluorescence studies.
- (3) Hydrochemical surveys.
- (4) Soil salts.
- (5) Determination of redox potential.
- (6) Bacterial methods.

As indicated in the title of the book prospecting ("poiski") is clearly distinguished from exploration ("razvedka"). In a summarizing chapter at the end of the book the methods

applying particularly to each of these are indicated, and an intermediate phase of the investigations is recognized:

Stages of work	Principal types of geochemical methods used
(1) Geological prospecting; reconnaissance work.	3, 1(c), 2
(2) Detailed geological prospecting and preliminary exploration.	3, 1(a), 1(b), 2, 6, 4, 5
(3) Exploration work (drilling for prospecting and structure purposes)	1(d), 2(b), 3

The Appendix is a useful generalized geologic column for the oil-producing regions of the U.S.S.R. The conventional eras, systems and series are given in three columns; the fourth column gives the names of forty-nine post-Devonian stages that are used in petroliferous areas in Russia.

It is surprising that no use has been made, either in the U.S.A. or the U.S.S.R., of the radiocarbon method to distinguish the hydrocarbons of soils and sub-soils that are formed by decomposition of modern organic material. Also, that determinations of helium or He^3/He^4 ratios are not mentioned in the book. Perhaps the gases of the exploited fields of the U.S.S.R. do not contain helium. Neither does the book mention any other studies of isotope ratios that might be useful in prospecting or exploration, although isotope geology is well advanced in the U.S.S.R.

This book is well written, clearly translated and certainly is the most comprehensive and detailed treatment of the subject available in any language. Its contents will give a good foundation for any individual or organization interested in the theory and practice of geochemical prospecting and exploration for petroleum and natural gas.

EARL INGERSON

A. FERSMAN: **Geochemistry for Everyone**. Translated from the Russian edition of 1948 by DAVID A. MYSHNE. Foreign Languages Publishing House, Moscow, 1958. 454 pp.

IN 1928 FERSMAN wrote a book called *Mineralogy for Everyone* as an experiment in introducing this science to school children and the interested layman. It was so successful that it was translated into many languages and ran twenty-five editions (printings?). This reception encouraged FERSMAN to write similar books, such as *Recollections about a Stone* (published in 1940), and at the time of his death in 1945 he was engaged in the more difficult task of bringing the new and complex subject of geochemistry to the same audience in the book under review. Chapters remaining unfinished were completed by his friends and colleagues as follows: "World of the Invisible" and "The Atom Disintegrates", by V. KHLOPIN; "Carbon — Basis of all Life" and "Atoms in Water", by A. P. VINOGRADOV; "Rare and Dispersed Elements", by V. V. SHCHERBINA; "Atoms in the History of Mankind", by N. RAZUMOVSKY; and "From the History of Geochemical Ideas", by D. SHCHERBAKOV, who also wrote the Foreword for the book.

This volume is not intended as a systematic or comprehensive treatment of geochemistry, but as a work to inspire high school students to go on and acquire a more complete knowledge of the subject by further study. The book is divided into four parts: The Atom, Chemical

Elements in Nature, History of the Atom in Nature, and Past and Future of Geochemistry, with a fifty-two page supplement giving a brief account of geochemical field work, brief information about each of the elements, and a glossary of geochemical terms.

Neither is the treatment of the individual elements systematic. There are separate chapters for fifteen elements, chosen more for interest than for geochemical importance and arranged in no particular order, and one short chapter giving a few facts about each of fifteen other elements. Fluorine and gold, for example, rate a chapter each, but hydrogen and oxygen do not. Chapter headings are designed to attract attention: "Phosphorus — Element of Life and Thought", "Strontium — Metal of Red Lights", Fluorine — the Omniverous", "Beryllium — Metal of the Future", etc. In addition to the numerous conventional illustrations in the text most of the page margins are illustrated with sketches ranging from miniature portraits of eminent scientists through drawings of fossils, plants, and minerals to cartoons of atoms performing their multitudinous and sometimes nefarious functions; e.g. oxygen atoms gleefully taking bites out of a railroad rail.

There are no abundance data for the elements and little systematic information about their geochemistry (the geochemical cycle of carbon is diagrammed and discussed). For the most part the chapters on elements are collections of interesting facts and stories about their occurrence, production and uses. The compositions of the atmosphere and oceans are given in detail, but the only information on the composition of the lithosphere is a list of the percentages of the nine most abundant elements of the upper 16 km of the crust.

Geochemistry for Everyone is authoritative and interestingly written. It is excellent for the purpose for which it was intended but, as is evident from the above remarks, it would not be appropriate for a textbook of geochemistry even in high school. For collateral reading in geochemistry for a high school course in geology or earth science it would serve admirably to inform and inspire the students—especially if the school library contained text or reference books on geochemistry so that the really interested students could fill in the gaps.

The University of Texas

EARL INGERSON

R. L. BATES: **Geology of the Industrial Rocks and Minerals** Harper and Brothers, New York, 1959. 441 pp. \$10.00.

A CAREFULLY chosen group of "non-metallic" deposits, representative of most genetic types and many economic types, is discussed from the geologic point of view. The treatment is up to date and as thorough as can reasonably be expected of a book of this scope. The arrangement of the material according to the proposed classification is as logical as any which has been applied to this diverse subject matter. The many references at the ends of sections will be especially appreciated.

An excellent text for undergraduates, the book is also useful as beginning point and unifying element for graduate study.

JAMES H. DAVIS

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